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Maximum Utilization of Water Resources in a Planned Community: Contributions of Refractory Compounds by a Developing Community

Rice Univ.
Houston, TX

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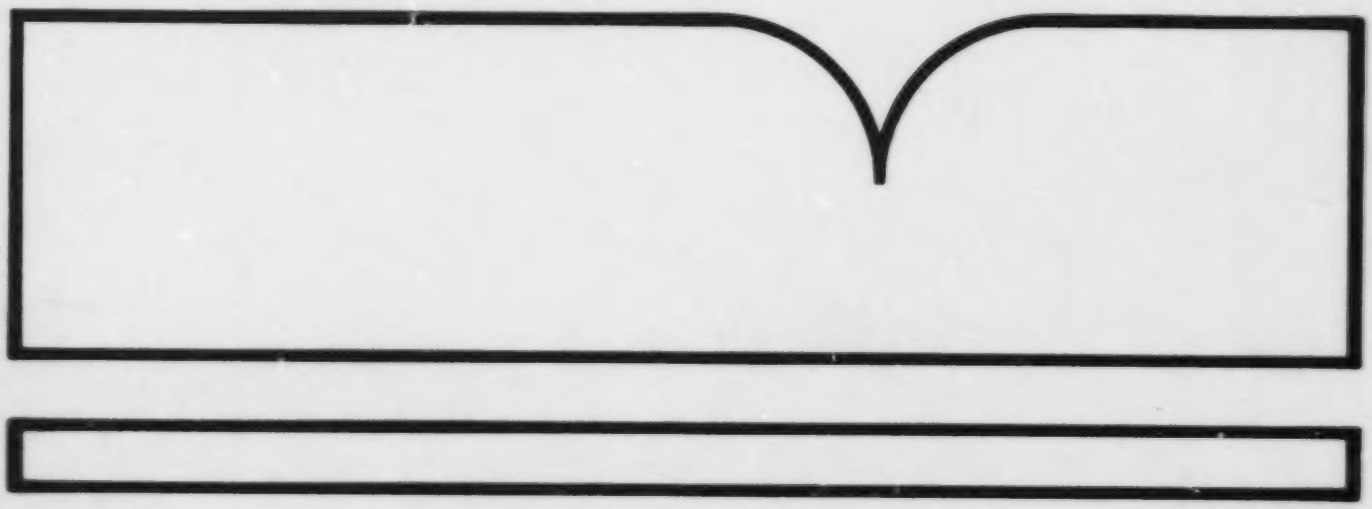

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Maximum Utilization of Water Resources in a Planned Community

Contributions of Refractory Compounds by a Developing Community

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16. ABSTRACT

Water, soil and biotic components from a natural drainage system in The Woodlands, a developing community in Texas, were assayed for halogenated compounds. PCB's were highest during year one (about 350 ppb in soil and animal samples) and diminished to 1/10 of those values during the second and third years of study. The highest residue values were coincident with the period of development when cut and fill operations, roadbed construction, and service installation were being effected. Mirex and chlordane were found in soil, water and organisms from the drainage system around the golf course. These were also observed compounds in mosquitofish collected from the same area. Both compounds entered lakes by storm water and/or washed in by returning irrigation water from the golf course. Organisms from a stream which received storm waters from the lakes contained less insecticide than the golf course sampling. The data suggest that biotic and abiotic components of the lakes may serve as effective "sumps" for these pesticides.

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MAXIMUM UTILIZATION OF WATER RESOURCES IN A PLANNED COMMUNITY

Contributions of Refractory Compounds by a Developing Community

by

F. M. Fisher
Department of Biology
Rice University
Houston, Texas 77001

Grant No. 802433

Project Officers

Richard Field
Anthony N. Tafuri
Storm and Combined Sewer Section
Wastewater Research Division
Municipal Environmental Research Laboratory (Cincinnati)
Edison, New Jersey 08817

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

The research reported here describes the role of a developing community in contributing refractory organochlorine compounds to the aquatic ecosystem. Water, soil, and biotic components from a natural drainage system in The Woodlands, Texas, were assayed over a 38-month period from 1973 to 1976.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

PREFACE

The overall goal of this research was to evaluate the water resource plan for The Woodlands, Texas, and to made recommendations, as necessary, to maximize its effective utilization through alterations in design and management. Any recommended alterations were to be critically evaluated as to their compatibility with the natural environment.

Collection and utilization of stormwater runoff for recreational and aesthetic purposes was a major feature of the water resources plan at The Woodlands. Control of downstream flooding was also of great importance and so storage reservoirs, in the form of recreational lakes and wet weather ponds, were created by the developers. Water quality was a concern if the impoundments were to be aesthetically appealing and/or suitable for recreation. Therefore, a major sampling and analytical program was designed to monitor water quality and quantity at different locations in the developing area. The Storm Water Management Model (SWMM) provided the focal point for combining the water quality and quantity data into a predictive tool for design and management purposes.

SWMM was originally developed for highly urbanized areas and, therefore, was calibrated for this project in an urban watershed (Hunting Bayou). Subsequently, SWMM was modified to model runoff and water quality from natural drainage areas, such as The Woodlands. Because of the lag in the construction schedule at The Woodlands, the dense urban areas were not completed during the project period. Consequently, Hunting Bayou and other urban watersheds were sampled to provide a basis for predicting pollutant loads at The Woodlands in the fully developed state.

Water analyses included many traditional physical, chemical, and biological parameters used in water quality surveys. Pathogenic bacteria were also enumerated since the role of traditional bacterial indicators in stormwater runoff was not clear. Algal bioassay tests on stormwater were conducted to assess the eutrophication potential that would exist in the stormwater impoundments. The source, transport, and fate of chlorinated hydrocarbons in stormwater runoff were also investigated.

Several of the large Woodlands impoundments will receive reclaimed wastewater as the major input during dry weather.

Besides their use as a source of irrigation water, the lakes will be used for non-contact recreation--primarily fishing and boating. Because the reclaimed wastewater must be disinfected, there was a concern about disinfectant toxicity to the aquatic life in the lakes. Consequently, comparative fish toxicity tests were conducted with ozone and chlorine, the two alternatives available at the water reclamation plant.

Porous pavement was considered by the developers as a method for reducing excessive runoff due to urbanization and an experimental parking lot was constructed. Hydraulic data were collected and used to develop a model compatible with SWMM, to predict the effects of using porous pavement in development. Water quality changes due to infiltration through the paving were also determined.

Hopefully, the results of this project will contribute in a positive way to the development of techniques to utilize our urban water resources in a manner more compatible with our cherished natural environment.

ABSTRACT

This project was undertaken to examine the role of a developing community in contributing refractory organochlorine compounds to the aquatic ecosystem.

Water, soil, and biotic components from a natural drainage system in The Woodlands were assayed for halogenated compounds by gas-liquid chromatography. In addition, components from two man-made lakes and the recipient stream were evaluated.

Polychlorinated biphenyl (PCB) residues were detected during each year of the three-year study. The levels of PCBs were highest during the first year (about 350 ppb in soil and animal samples) and diminished to 1/10 of those values during the second and third years of study. The highest residue values were coincident with the period of development when cut and fill operations, roadbed construction, and service installation were being effected.

The chlorinated camphene, mirex, which is used for fire ant control was found in soil, water, and organisms from the drainage area around The Woodlands Golf Course as were residues of chlordane. The presence of these refractory compounds in the water and soil was reflected in samples of mosquitofish collected in the same area.

Although the pesticide levels in fish were highest around The Woodlands Golf Course, the level never exceeded 5.6 ppb for mirex and 6.1 ppb for chlordane. Both compounds were apparently transported into the Conference Center Lakes by stormwater and/or washed in by returning irrigation water from the golf course. Fish from Panther Branch, which receives stormwaters from overflow of the Conference Center Lakes, contained less than one-fourth the amount of mirex and chlordane found in golf course samplings. The data indicated that biotic and abiotic components of the lakes serve as effective "sumps" for these pesticides.

This report was submitted in partial fulfillment of Grant No. 802433 by Rice University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from September 1, 1973 to December 15, 1976, and work was completed as of March 15, 1977.

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ABBREVIATIONS

Aldrin	-- 1,2,3,4,10,10-hexachloro-1,4,4',5,8,8'-hexahydro 1,4-endo, exo 5,8 dimethanophthalene
Chlordane	-- 1,2,4,5,6,7,8,8-octachloro-2,3,3',4,7,7'-hexahydro-4,7-methanoindene
O,P.DDD	-- -2-(0-chlorophenyl)-2-(p-chloro-phenyl)-1,1-dichloroethane
p,p-DDD	-- 2,2-bis(p-chlorophenyl)-1,1-dichloroethane
p,p-DDE	-- 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene
p,p-DDT	-- 1,1,1-trichloro 2,2-bis(p-chlorophenyl)ethane
Dieldrin	-- 1,2,3,4,10,10'-hexachloro-6,7-epoxy 1,4,5',5,6,7,8,8' octahydro-1-4-endo,exo-5,8-dimethano-naphthalene
Heptachlor	-- 1,4,5,6,7,8,8'-heptachloro-3',4,7,7'-tetrahydro 4,7-methanoindene
Heptachlor epoxide	-- 1,4,5,6,7,8,8'-heptachloro-2,3-epoxy-3',4,7,7' tetrahydro-4,7 methanoindene
Lindane	-- gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane
Mirex	-- Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta(cd) pentalene
PCB	-- polychlorinated biphenyl
Toxaphene	-- a mixture of chlorinated camphenes
GLC	-- Gas-liquid chromatography
ppb	-- parts per billion
ppm	-- parts per million
CCM	-- Conference Center Marsh

ACKNOWLEDGMENTS

The Woodlands, a developing community north of Houston, Texas, is gratefully acknowledged for their cooperation and interest in this project. The research group of the Environmental Science and Engineering Department at Rice University collected some abiotic samples for this phase of the study.

SECTION 1

INTRODUCTION

The name chlorinated hydrocarbon has been loosely applied to a group of synthetic organochlorine compounds which share certain qualities, the most important of which is an insecticidal action; or as Moore (1) more accurately described it, a "biocidal" action. With few exceptions, the chlorinated hydrocarbon insecticides also share the properties of a broad spectrum of insecticidal action, relatively simple structure (promoting ease of manufacture), prolonged stability and residual action, and relatively low mammalian toxicity (2). Highly insoluble in water, most organochlorine insecticides share the property of high lipid solubility. Though the exact mode of action of these compounds is not known, it is generally thought that they act on cell membrane surfaces, a theory which the lipid nature of membranes would seem to support. Metcalf (2) suggested that DDT disorders the surface membranes of nerves affecting calcium permeability, and O'Brien (3) speculated that cyclodiene insecticides acted similarly by complexing with neural membranes in such a way as to modify their properties. Since cell membranes are common to all living organisms, it would appear that organochlorine formulations do possess the potential of being biocidal.

The persistence and biomagnification of chlorinated hydrocarbons in the environment are the principal factors which have led to a decline in usage. Available commercially only since 1945, DDT has been detected in remote regions of the globe and the discovery that marine fish are almost universally contaminated with DDT residues are testimony to the problems of persistence and biomagnification. Since lower animals serve as food for the higher animals, the chlorinated hydrocarbon content in fatty tissue tends to increase in concentration as one moves up the food web. The discovery of DDT in human milk (4) suggests that man is not immune to the process of biomagnification.

The problem of contamination is a unique environmental situation in that pesticides are deliberately introduced for beneficial and/or monetary purposes. They are not for the most part waste products as is characteristic of the large majority of environmental contaminants. Though initially introduced into an agricultural or urban ecosystem in a controlled manner to eliminate a target species, the action and fate of persistent compounds are neither simple nor controlled, but rather complex and

uncontrolled. The reasons for this are numerous: first, the organochlorine compounds are not selective in their action for a single pest species; instead they demonstrate a broad spectrum of biocidal action. In order to reach the target organism, all other organisms and components of the system are subjected to the chemical.

One of the first components of an ecosystem to come in contact with an organochlorine formulation is the soil. The behavior of such residues in soils has been the subject of numerous investigations. The persistence of these refractory compounds is dependent on such factors as concentration (5), volatility (6), temperature (7), organic content of soil (8), clay and moisture content (9), and usage of soil (10).

The long life of chlorinated hydrocarbon residues is compounded by extremely slow diffusion of the compounds through soil. Over 80% of the chlordane and dieldrin residues remain in the top 10 cm of soil ten years after application. Leaching of such compounds into subsurface waters does not therefore present a particular problem. What then is the fate of such refractory compounds in soil? Two major pathways of dieldrin loss from soil are volatilization and sediment transport, but the amounts dissolved in runoff water and absorption by vegetation may be significant (11). Though only very slightly soluble in water, chlorinated hydrocarbon compounds enter waterways dissolved in minute amounts or in much greater amounts adsorbed onto suspended sediment particles (12). Certainly, the primary means whereby toxic residues are transported from one area to another is water and compounds need not be in solution for such transport. It is this presence of residues in surface waters that exposes yet another biological community to chlorinated compounds. Numerous non-target arthropods, molluscs, fish, and algae are sensitive to these formulations (13). It is a fact that most populations of organisms in the world have exhibited no readily visible effects from contact with chlorinated hydrocarbon compounds, but it does not suffice to assume that there are none. Certainly, acute effects of some formulations have produced kills of non-target organisms following ingestion or absorption. However, the effects most common and difficult to assess are the sub-lethal effects, i.,e., effects due to any dose of a compound below that which produces death. Growth retardation may be attributed to chlorinated hydrocarbon exposure (12,14,15,16,17, 18). Somewhat more subtle effects of chlorinated hydrocarbons have been noted on metabolism and growth at the cellular level where long-term effects can be classified as carcinogenic, teratogenic, or mutagenic.

A basic principle of ecology is that no component of an ecological system can be altered without affecting the whole system. Any factor or factors that affect even so much as a single organism or component will produce an effect on the system as a

whole. As Moore (1) pointed out, no plant or animal lives in isolation. An application of a chlorinated hydrocarbon never results in a total reaction of the form:

Pesticide → Pest

All pesticide applications, in fact, consist of the reaction:

Pesticide → Ecosystem in Which Pest Lives

It has been predicted that stability of an ecosystem is correlated with diversity of organisms and that decreasing diversity leads to decreased stability (19). This idea is significant in light of research by Menhinick (20), who observed reduced diversity in areas of pesticide application.

At present some data exist on the distribution, location, and impact of pesticides in natural living systems. A hindrance in obtaining such information has been a lack of understanding of normal patterns and variations in biotic communities needed to serve as baseline for understanding pesticide pollution effects. Studies of halogenated hydrocarbon residues have been undertaken in relatively few complete systems. Freshwater marshes (21), freshwater streams (22), saltwater marshes (23,24), and brackish water marshes (25) have been examined.

In 1971 registration cancellation proceedings were initiated against the manufacturers of DDT, mirex, aldrin, and dieldrin. The subsequent ban on nearly all uses of DDT, aldrin, and dieldrin demonstrated the risk of the chlorinated hydrocarbon formulations to man and the environment. With the decreased usage of the refractory halogenated compounds, there has been a concomitant increase in the usage of the less persistent carbamate and organophosphorus formulations. Although these latter classes of pesticides have relatively short half-life in the environment, they exhibit, in general, greater acute toxicity to both vertebrates and invertebrates. It is important, therefore, to understand the routes and velocity of pesticide loss from treated areas and transport to aquatic environments. Such an understanding in concert with knowledges of the effects of nontarget species could provide an equitable basis for administration and regulation of these alternate chemicals.

Although not considered biocides, another group of chlorinated hydrocarbon compounds has been noted in the environment in recent years. The polychlorinated biphenyls (PCBs) have been used in industry for forty years. Under the trade name "Aroclor," these refractory compounds are involved in manufacturing as plasticizers, flame retardants, insulating fluids, and a host of other applications. As additives to many products, the "Aroclors" improve the quality of the product or material. Such is the case with printers ink, floor tile, electrical

products, synthetic rubber, varnishes, waxes, asphalt, and adhesives. The source of these compounds which consist of chlorobiphenyls or chloroterphenyls is many or varied and it is of some interest that at one time the addition of PCBs to chlorinated pesticides was suggested to suppress vaporization, therefore, extending their half-life. By the methods employed in this study, the PCBs were analyzed in a large number of biotic and abiotic samples.

There is, however, a paucity of information on chlorinated hydrocarbon contamination from urban ecosystems. This source of pollution is relevant in view of recent demographic trends which suggest that approximately 75% of the population in the United States will reside in a 100-mile band adjacent to the coastline by 1980 (26). Water from such centers of population often supply the freshwater component to important coastal estuarine ecosystems. One of the most important estuaries in the Texas Coastal Zone is the Galveston Bay Complex which receives major surface runoff via the San Jacinto and Trinity Rivers. Numerous small streams and bayous also contribute freshwater to this productive bay ecosystem. The Woodlands is located on Spring Creek which contributes surface water to the San Jacinto River drainage basin. That river not only supplies Galveston Bay with its riverine component, but also affords a major water supply to the City of Houston from a man-made impoundment, Lake Houston. One could not expect a developing community the size of The Woodlands to be especially significant in adding refractory compounds to this waterway; however, the location of The Woodlands in an area with little agricultural history suggests that there would be little or no background input of pollutants in the stormwaters. Hence, any measurements would be the result of urbanization or urban processes.

SECTION 2

SUMMARY OF RESULTS/CONCLUSIONS/RECOMMENDATIONS

CHLORINATED HYDROCARBON SURVEY

During the two and one-half year study, some 2,500 biotic and abiotic samples were collected in The Woodlands and analyzed for halogenated hydrocarbon compounds. The major emphasis was directed toward surface water (905) and aquatic fauna (899) samplings; however, 560 soil-sediment and 113 plant samples were also analyzed.

POLYCHLORINATED BIPHENYLS (PCBs)

1) The major class of chlorinated compounds detected during the study was the polychlorinated biphenyls (PCBs). These formulations are used in a variety of industrial applications such as varnishes, paints, inks, waxes, flooring tile, synthetic rubber, and asphalt; however, the greatest usage is in the electronics industry in the production of capacitors and transformers. The PCBs have been produced for over forty years but only recently have they been observed as a pollutant in the environment.

2) In January 1974, a sudden increase in the PCBs in soils (up to 341 ppb) was observed, which was followed by a rise in the concentration in surface waters (maximum of 8.2 ppb) some four months later. The rates of decline of both of these peak concentrations resemble a first order curve. No further increase in PCBs in water was observed throughout the remainder of the study. By extracting larger amounts of soil concentrating the compounds on activated charcoal followed by elution and subsequent analysis, a second minor peak was observed in soil samples during the spring of 1975. The peak in 1975 was three orders of magnitude lower than the major peak in 1974. Several plant samples were found to contain trace amounts of PCBs, but these minute amounts could have been due to surface contamination since they coincided with the highest values observed in water and soil samples. The level of PCBs in aquatic animal samples started rising in late 1973 and reached a peak (30 ppb) in April of 1974, which is coincident with about 3.0 ppb in the water samples. The concentration in the aquatic organisms is about 10 times that in the water samples but 1/10 that observed in the soil samples.

3) The source of the PCBs in The Woodlands is not known. It is of interest that the peak of PCBs in all components of the ecosystem appeared during a period of intense cut and fill operations as well as utility installation. An abandoned landfill with disposed capacitors or other electronic materials could have effected the increase in concentration, as could the use of road oil contaminated with PCBs. Neither of these thoughts were verified by observation. The use of PCBs in synthetic heat resistant oils, including hydraulic oils, may represent a possible source of this contamination. The highest level of PCBs was observed during a period where the maximum cut and fill operations were underway. The utilization of hydraulic systems or such equipment is well documented.

CHLORINATED HYDROCARBON PESTICIDES

1) Traces of DDE were observed in samples of crayfish, mosquitofish, and bluegills obtained from The Woodlands aquatic ecosystem during the first year of study. Following completion of recreational facilities such as the golf course, mirex and chlordane were found in soil and water samples associated with this facility.

2) In the spring of 1975, mirex was detected in water (to 15 ppb), soil (to 30 ppb), and some aquatic organisms (to 55 ppb). The highest values were found in the mosquitofish (55 ppb) and the lowest in water samples with the residue in soil being intermediate between the fish and water. If there was any biological amplification in the fish from this aquatic system, it was limited to about a four-fold increase over concentrations in the water. Water from the Conference Center Lakes (A & B) was used for irrigation of portions of the golf course. Since these manmade impoundments were the potential recipients of both irrigation and stormwater runoff, the lake water sediments and mosquitofish were examined for mirex. The highest level of mirex was observed in mid to late summer (1975), and thereafter the concentration of all three components of the pond ecosystem diminished rather rapidly with the soil residues showing the slowest rate of decline. The concentration of mirex in the lake aquatic system was at least one order of magnitude lower than that observed on or adjacent to the golf course. The lower concentration possibly being due to dilution and runoff.

3) During August of 1974, chlordane was also detected in the golf course study. Residues were found in soil, water, and aquatic organisms. The highest levels of chlordane were found in the crayfish (43 ppb) from golf course ponds. Somewhat less was observed in the same organism from ditches adjacent to the course. Similar, although not as pronounced, results were observed in the concentration of chlordane in the waters from the same areas.

CARBAMATE COMPOUNDS

Attempts were made to examine the runoff of a carbamate pesticide from an urban yard. Although the resemblance of a first order curve was obtained, it was unfortunate that the interpretation of the data was in error. Extract of runoff waters was examined by gas-liquid chromatography (GLC) prior to derivatization with trifloroacetic anhydride and the results were nearly identical with derivatized samples. During concurrent studies in a ricefield-marshland ecosystem, the same observations were made. Naturally occurring compounds often effect spurious peaks in GLC determinations, especially when electron capture detectors are employed. Solfur or sulfur-containing compounds are among the more notorious contaminants in producing such artifacts. Such contaminants can be removed from samples with bright copper or treatment with mercury.

MONITORING PROGRAMS

The present study reinforces the notion that monitoring programs for chlorinated hydrocarbon compounds should be continued. That such compounds appear and increase in amount with urbanization of a heretofore "pristine" area is sufficient argument for continued monitoring. Specifically, chlorinated hydrocarbon compounds should be monitored in The Woodlands on at least a biannual basis to follow the distribution of refractory compounds. Monitoring should be restricted to the Conference Center Lakes (A & B). These lakes receive runoff waters from the golf course, which appears to be a major source of insecticidal compounds at the present time. Since waters from these lakes are used for irrigation of the golf course, there is a possibility of reaching toxic levels of mirex and chlordane in lake sediments. If the lakes are to be used for any form of recreation, the monitoring schedule should be enhanced. At present, the lakes appear to be functioning as a "sump" for the above refractory compounds. All attempts should be instituted to prevent scouring and movement of the halogenated compounds downstream.

SECTION 3

RESULTS AND DISCUSSION

SAMPLING

During this 38-month study of surface waters in The Woodlands, some 2,500 biotic and abiotic samples were analyzed for halogenated hydrocarbon compounds and/or carbamate formulations. The major portion of these samples was collected in the drainage system within The Woodlands development. A resume of the samples by year and type of material examined is presented in Table 1.

TABLE 1. DISTRIBUTION OF SAMPLES BY YEAR AND TYPE OF MATERIAL ANALYZED

Type of Sample	1973-74	1974-75	1975-76	Total
Water	513	270	122	905
Soil	182	270	108	560
Animal	376	438	85	899
Plant	73	40	0	113
TOTAL	1,144	1,018	315	2,477

Considerably more attention was directed toward the analysis of water (905) and animals (899); however, 560 soil-sediment (herein referred to as soil) and 113 plant samples were also analyzed. The experimental procedures are presented in Appendix A. The major number of samples were collected from sites along the the major waterways in or adjacent to the development (Figure 1).

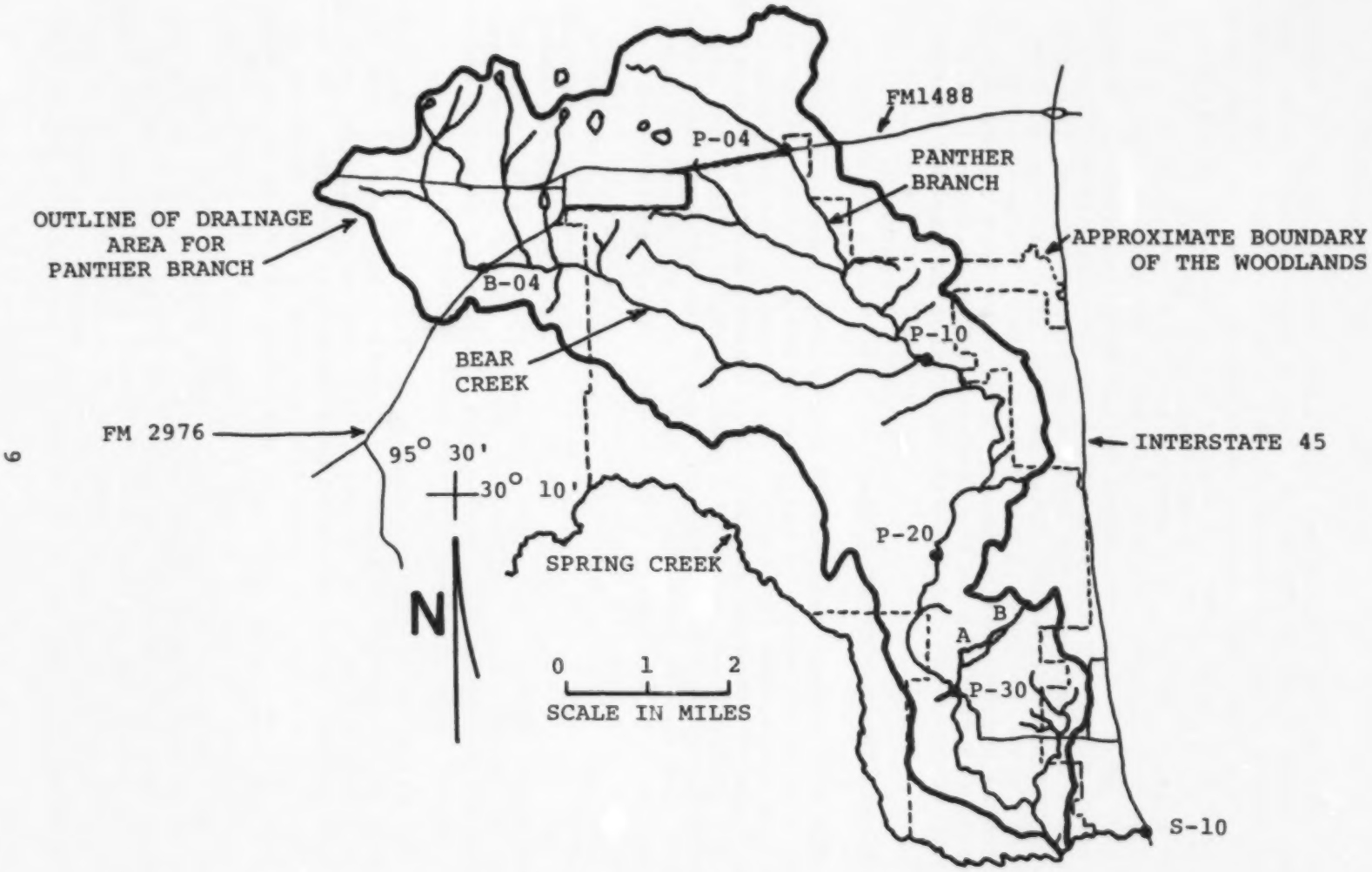

Figure 1. Map of sampling locations in The Woodlands waterways.

Initially, four sampling locations were selected on Panther Branch (P-04, P-10, P-20, P-30), one on Bear Branch (B-03), and one on Spring Creek at Interstate 45 (S-10). Lakes A and B (A,B) as well as a transient freshwater marsh (M) near the headwaters of Lake B were also examined during the first year of study. With the exception of the freshwater marsh (M) and the Bear Branch station (B-03), all study sites were continued during the second year of study. During this phase of development, The Woodlands Golf Course was added to the sampling regime. This was considered necessary since waters from the Conference Center Lakes (A & B) were used for irrigation of portions of the golf course. Excess irrigation water as well as storm runoff from the golf course re-entered the lake system. The monitoring of halogenated hydrocarbon compounds during the last six months of the study was confined to the Conference Center Lakes (A & B), the golf course, and the downstream station on Panther Branch (P-30).

POLYCHLORINATED BIPHENYLS (PCBs)

The most common halogenated hydrocarbon compounds identified during this study were the polychlorinated biphenyls (PCBs) sold under the trade name "Aroclor." The resumé of the polychlorinated biphenyl residues in soil is presented in Table 2 where the data are arranged according to sampling sites. The upper portions of the watershed of Panther Branch are of particular interest. The two sampling points near the western and northern boundary of The Woodlands, B-04 on Bear Branch and P-04 on Panther Branch, display quite different quantities of PCBs in soil samples. Samples from Bear Branch (B-04) analyzed during late 1973 and the first half of 1974 did not have any appreciable PCBs; however, corresponding samples from Panther Branch (P-04) had residues ranging from trace amounts (less than 0.5 ppb) to 97 ppb during the same collection period. Based on these observations, B-04 was deleted during the second year of study and replaced with P-10 downstream from P-04 (Figure 1).

The first three monthly samples at P-04 (September through November 1973) did not contain sufficient quantities of PCBs to obtain quantitative data; however, the samples collected over the next six months contained residues approaching 100 ppb. It is also of interest that elevated residue levels were observed at stations P-20 and P-30 (Table 2) some five and seven miles downstream within The Woodlands (Figure 1). It would appear that this particular incident of PCB introduction came from outside of The Woodlands. During this same time period, PCBs also appeared in soil samples from Lakes A & B (Table 2). It is improbable that the residues in Lakes A & B are associated with the pollution event in the Panther Branch system since the lakes are located about 0.4 miles upstream from Panther Branch (Figures 2 and 3). The residue analysis of soil samples throughout the remainder of 1974 failed to disclose any appreciable quantities

of PCBs (Table 2). During the spring of 1975, there was a minor occurrence of PCBs in the Panther Branch system and did not involve Lakes A & B (Table 2). Small amounts of PCBs were present in soil from P-04 for several months and corresponding values were also recorded at P-10 some three miles downstream from P-04. The residues were also recorded at P-20, P-30 and S-10, the station at Spring Creek and I-45.

TABLE 2. POLYCHLORINATED BIPHENYL RESIDUES IN SOIL SAMPLES (ppb)

Year/ Month	Collection Site								
	B-04	P-04	P-10	P-20	P-30	S-10	Lake A	Lake B	Marsh
1973/S	Tr	Tr		NS	Tr	ND	Tr	Tr	ND
O	Tr	Tr		Tr	Tr	Tr	ND	Tr	ND
N	NS	Tr		NS	Tr	ND	1.0	Tr	ND
D	NS	73.0		NS	51.0	10.0	1.0	13.0	Tr
1974/J	Tr	80.0		Tr	Tr	Tr	Tr	Tr	3.1
F	Tr	90.2		80.0	341.0	Tr	92.0	NS	NS
M	NS	97.0		130.0	200.0	Tr	239.	NS	16.0
A	Tr	83.0		172.0	54.0	4.0	170.	161.0	ND
M	Tr	92.0		30.0	Tr	Tr	120.	173.	ND
J	NS	Tr		NS	Tr	Tr	Tr	130.0	NS
J	NS	NS		NS	NS	NS	NS	NS	NS
A		1.1	0.8	2.1	1.0	2.1	0.8	1.1	
S		1.8	1.4	1.7	0.9	Tr	Tr	0.9	
O		Tr	1.0	1.1	0.7	Tr	Tr	0.7	
N		1.5	1.3	0.7	1.0	Tr	1.0	Tr	
D		1.1	1.0	0.9	1.9	1.0	Tr	0.8	
1975/J		1.3	1.0	1.0	1.0	1.0	1.2	1.2	
F		1.1	0.8	Tr	0.8	1.4	Tr	0.7	
M		1.5	2.1	2.0	1.6	3.1	0.7	0.9	
A		1.2	1.7	1.7	1.1	3.6	0.7	0.8	
M		1.0	0.8	0.9	Tr	2.1	1.0	1.2	
J					1.0		1.1	1.2	
J					1.4		1.3	1.1	
A					1.7		0.9	1.0	
S					0.9		0.9	1.0	
O					1.0		ND	Tr	
N					Tr		ND	Tr	
D					0.9		Tr	Tr	

Tr = Trace

ND = Not detected

NS = No sample

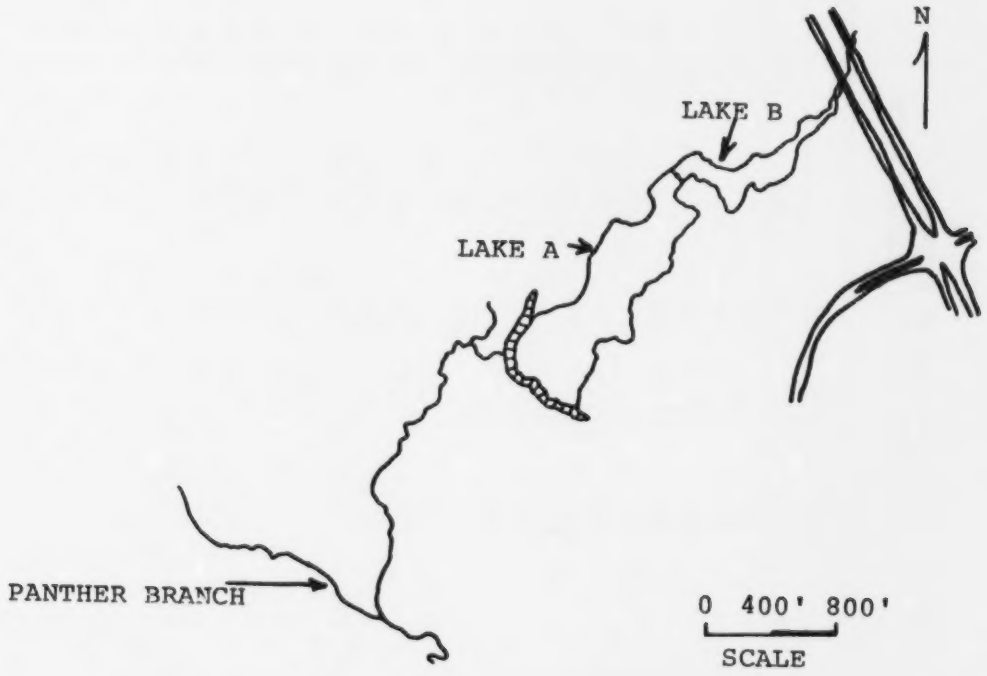

Figure 2. Map of Lakes A & B indicating the freshwater marsh and relationship of the lakes and marsh to Panther Branch.

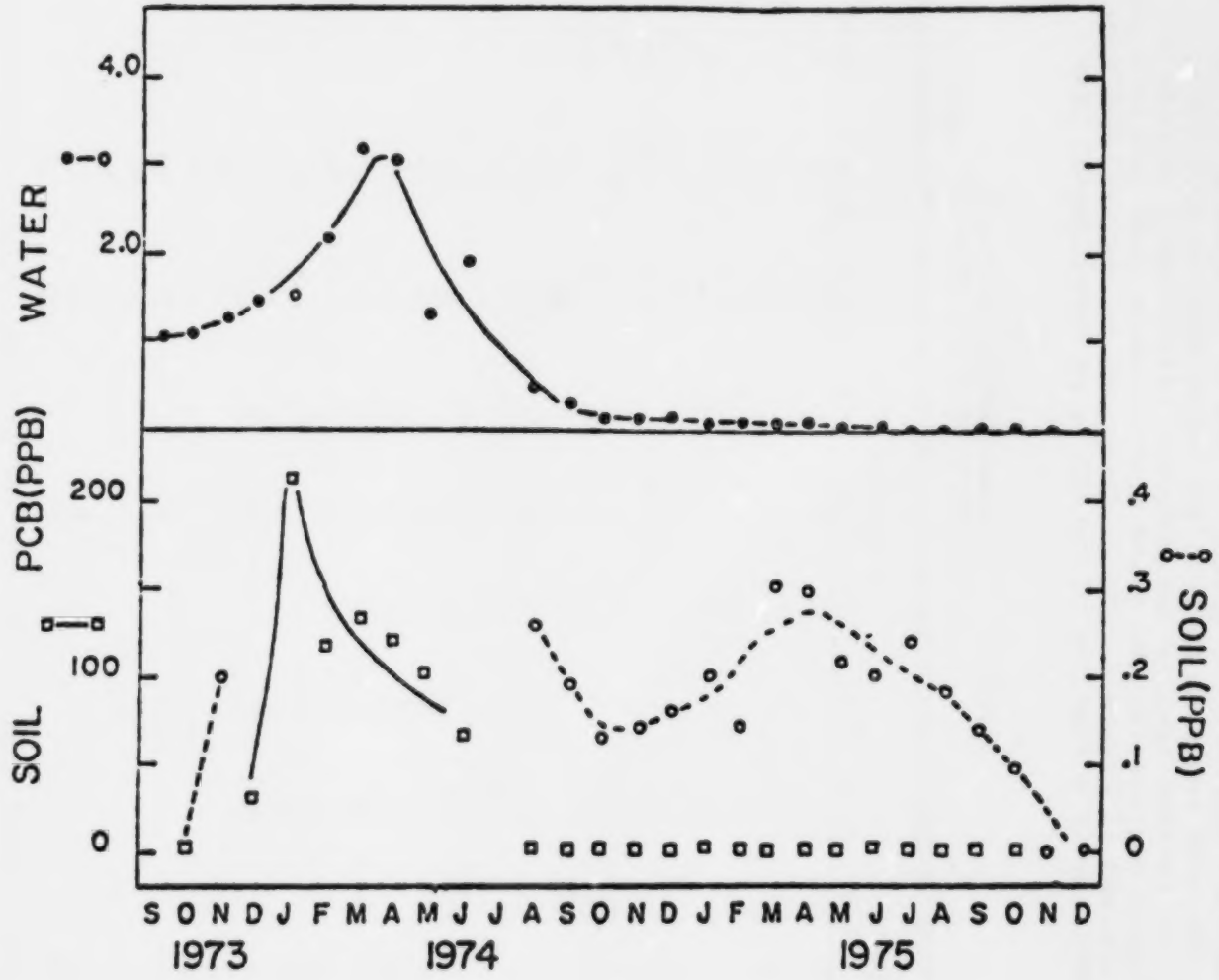

Figure 3. Temporal distribution of polychlorinated biphenyls in The Woodlands.

The concentration of PCBs in water never approached that measured in soil samples (Table 3). The observation of PCBs in soil samples (early 1974, Table 2) appears to be reflected in water samples from Panther Branch at nearly the same sampling time. The same seems to be true for water samples from Lakes A & B. To further examine the temporal relationship of PCBs in the abiotic components, the grand monthly means from Tables 2 and 3 are slotted in Figure 3. It is important to realize that biocide mobility is a function of runoff in an experimental area.

TABLE 3. POLYCHLORINATED BIPHENYL RESIDUES IN WATER SAMPLES (ppb)

Year/Month	Collection Sites								
	B-04	P-04	P-10	P-20	P-30	S-10	Lake A	Lake B	Marsh
1973/S	Tr	Tr		Tr	1.2	Tr	Tr	ND	1.0
O	Tr	1.1		Tr	1.3	Tr	ND	ND	ND
N	Tr	1.0		ND	Tr	1.1	1.9	Tr	1.3
D	ND	Tr		ND	1.1	1.2	2.0	2.0	1.2
1974/J	Tr	Tr		Tr	1.0	Tr	2.1	Tr	Tr
F	1.9	1.2		1.6	3.6	Tr	Tr	Tr	2.1
M	Tr	Tr		2.1	1.5	1.1	8.2	2.5	Tr
A	1.2	1.2		2.3	4.8	1.2	6.1	2.1	Tr
M	Tr	Tr		1.4	1.1	1.1	1.0	1.1	2.0
J	ND	1.0		1.4	3.4	Tr	ND	NS	1.2
J	NS	NS		NS	NS	NS	NS	NS	NS
A		2.1	Tr	Tr	Tr	Tr	Tr	0.8	
S		1.0	Tr	Tr	Tr	Tr	Tr	0.5	
O		Tr	Tr	Tr	Tr	Tr	Tr	Tr	
N		Tr	Tr	Tr	Tr	Tr	Tr	Tr	
D		Tr	Tr	Tr	Tr	Tr	Tr	Tr	
1975/J		Tr	Tr	Tr	Tr	Tr	Tr	Tr	
F		Tr	Tr	Tr	Tr	Tr	Tr	Tr	
M		Tr	Tr	0.7	Tr	Tr	0.5	Tr	
A		Tr	Tr	Tr	Tr	Tr	0.6	0.7	
M		Tr	Tr	Tr	Tr	Tr	Tr	0.9	
J					Tr		Tr	ND	
J					Tr		Tr	Tr	
A					0.5		Tr	ND	
S					0.6		ND	ND	
O					0.5		ND	Tr	
N					Tr		ND	ND	
D					Tr		ND	ND	

Tr = Trace

ND = Not detected

NS = No sample

In an ecosystem as large and diverse as The Woodlands it is difficult, if not impossible, to examine this parameter without time averaging. The areas of application are minute compared with the magnitude of the watershed and the intensity of rainfall in concert with the natural slope result in a highly erratic flow in the waterways. Standing or permanent water is restricted to two lakes and these are subject to great turnover during modest rainfall. These climatic and topographical features are complexed with the extreme amount of sediment burden in stormwaters and the natural rates of decomposition of the applied biocides.

In ideal situations following application of a pesticide, a first order decay curve is commonly observed (13); however, these results are predicated to a great degree on time averaging of the runoff system. Inherent in such an ideal system is a standing water basin, a watershed with little slope, and slow or impeded runoff. To gain an overall representation of the temporal flux of PCBs in The Woodlands, the data from all sampling stations in the watershed are plotted versus time of year. This rationale in the treatment of these data is presented in Figure 3. As can be seen, the peak concentration in the water appears during March and April of 1974, while the highest value for soil residues appears in January of 1975. Since PCBs and most clorinated compounds are strongly adsorbed to sediments, it appears that there is a gradual release of the compounds to the stream waters. Two ordinal scales are presented for the soil data. The highest concentration in PCBs was in late 1973 and early 1974, with a minor peak in 1975 which was three orders of magnitude lower than the 1973-74 peak.

The source of the PCBs in this study remains unknown. The major use of the "Aroclors" is in the manufacture of capacitors and transformers. Many paints and varnishes contain PCBs, as do wax, printers ink, flooring tile, synthetic rubber, and asphalt. The wide usage and their new ubiquitous occurrence in the environment have only recently been known. It is of interest that the major cut and fill operations for roadway construction were underway during the observed peak of PCBs. Utility installation was also being accomplished at the same time.

PCB residues were not observed in plant sampling in measurable quantities; however, several samples were found to have trace quantities (<0.5 ppb). These samples coincided with the highest values recorded in Figure 3. The chemical nature of the halogenated hydrocarbon compounds suggests that the few plant samples were contaminated externally with PCBs.

The PCB levels in aquatic animal samples reached the highest levels in late 1973 and early 1974 (Table 4). The grand mean of these values is about 40 ppb. Examination of the temporal distribution of these compounds (Figure 4) reveals that the elevated levels in three species of aquatic organisms, mosquitofish, bluegill, and crayfish, superimpose with the highest concen-

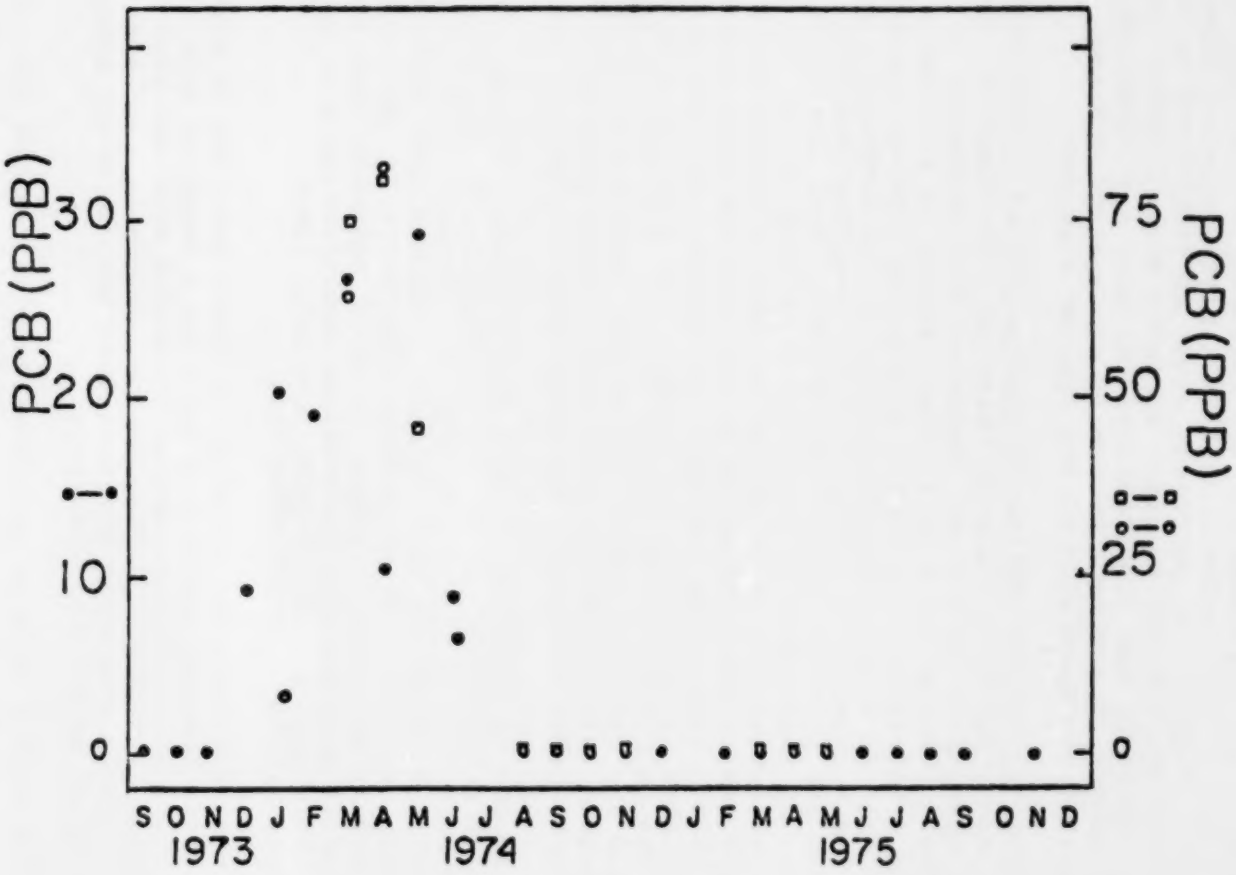

Figure 4. Temporal distribution of polychlorinated biphenyls in aquatic fauna in The Woodlands.
●-● mosquitofish (Gambusia sp.); □-□ bluegill (Lepomis sp.); o-o crayfish (Cambarus sp.).

trations in soil and water (Figure 3). The levels of PCBs in mosquitofish and crayfish samples examined during the second year of study were much lower than those in year one. The values obtained with the sample size used necessitated concentrating the sample with activated charcoal and elution of the material from the absorbent. During this procedure some naturally occurring electron dense compounds are concentrated and, therefore, interfere with the quantitative results. The data (Figure 4) during the second half of 1974 and 1975 were obtained by this technique. Even though these samples were concentrated, the values are still low compared with the data obtained in late 1973 and early 1974. The important consideration is that the introduction of a refractory material into the environment results in the passage of that component through various components of the ecosystem.

TABLE 4. POLYCHLORINATED BIPHENYL RESIDUES IN ALL ANIMAL SAMPLES (1/1/73 - 6/30/74)

Location	%Positive	Average & Range (ppm)
B-04	17	Tr
P-04	61	121.8 (1.3-250)
P-20	58	7.0 7.0
P-30	53	3.1 (1.1-4.6)
S-10	39	1.3 (1.0-1.7)
Lake A	75	20.7 (1.7-62.0)
Lake B	100	42.5 (36-49.1)
Marsh (M)	81	110.9 (32-300)

The source of the PCBs in this ecosystem remains obscure, but it is of interest that the major amount of cut and fill operations was underway when the peak in concentration was observed. There was also a great amount of utility installation occurring at this time. With the heavy usage of PCBs in capacitors for electric motors, florescent lighting, etc., it is possible that an abandoned disposal area was encountered during the cut and fill operations. PCBs have also been incorporated in road oils and if such were used to control dust problems, these would contribute to the peak in concentration in early 1974. No observations confirming these assumptions were made.

CHLORINATED HYDROCARBON PESTICIDES

During the first year of this investigation, trace levels of DDE were found in samples of crayfish and mosquitofish from stations P-04 and P-30 on Panther Branch. Mosquitofish collected from Lake A and the freshwater marsh (M) also contained trace

amounts of DDE. The station on Spring Creek (S-10), which receives the combined runoff from Panther Branch and Lakes A & B, yielded crayfish which contained DDE residues. With the exception of the samplings at S-10 and the freshwater marsh, all stations yielded trace amounts as early as October 1973. Confirmation of the DDE in these samples was effected by utilization of two-column analysis, binary solvent extraction, and cochromatography with authentic DDE standards.

The cyclodiene pesticide, dieldrin, which is the epoxide of aldrin, was recovered in fish and crustacean samples from stations on Panther Branch. Samples of bluegill from P-04 contained trace amounts of dieldrin, whereas samples of crayfish and bluegills collected at P-30 contained from trace amounts to 2.1 ppb of that compund. The mosquitofish (Gambusia sp.) was the only organism from Lake A which contained dieldrin. Values from trace amounts to 11.3 ppb were recorded in samples of this fish.

Following completion of The Woodlands Golf Course, the ephemeral water on the course, ponds, and adjacent ditches were examined for chlorinated hydrocarbon pesticides. During the spring of 1975, mirex, a chlorinated camphene, was first observed in the water, soil, and mosquitofish samples. The results of the study of this portion of The Woodlands watershed are presented in Figure 5, where the grand means of all samples from the golf course are plotted against the time of year. Highest amounts of mirex appeared during the months of July, August, and September. Water samples contained the smallest amount, followed by soil samples which contained about two times as much mirex as the covering water. Of particular interest is that the residue levels found in the mosquitofish reached an average level of twice that in the soil samples (Figure 5).

Mirex at the time of this investigation was used locally in the Gulf Coast States for the control of the fire ant (Solenopsis), a troublesome species accidently introduced into the United States from Argentina. It is commonly applied on wheat brand or similair food stuff which the ant consumes. Spring and summer were the common periods of treatment for this pest. It is suggested from the data presented in Figure 5 that this compound can undergo biological amplification in a rather restricted environment such as a golf course. At this writing it is, however, impossible to state how the mosquitofish obtained the compound, i.e., via the food web or by direct absorption from the water. The latter route has been illucidated by several investigators (25,30,31). In particular, Murphy (31) stresses the point that gill absorption is important in small fish where the ratio of gill surface to body weight is large. Certainly, mosquitofish would fall into this category.

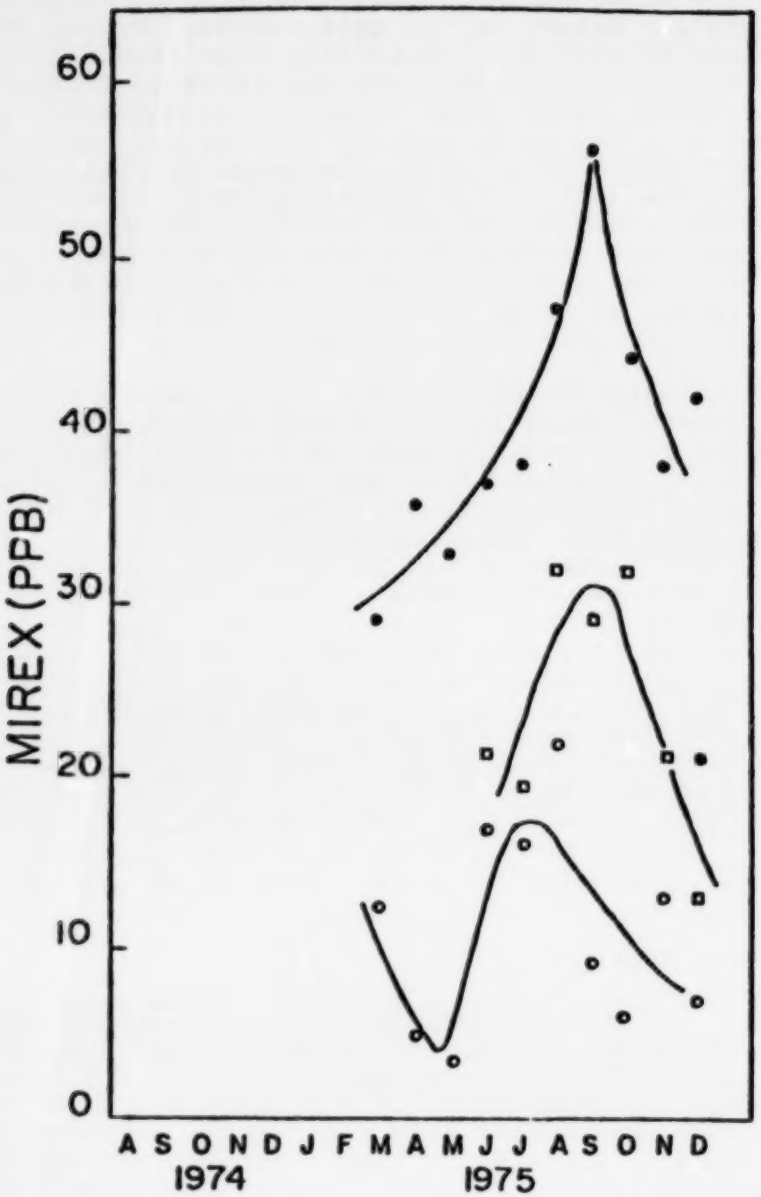

Figure 5. Temporal distribution of mirex in The Woodlands Golf Course. ●-● mosquitofish (Gambusia sp.); ▫-▫ soil; o-o water.

During the drier months of 1975, water from Lakes A & B was used as irrigation water for the golf course. During such a practice, there existed the possibility that return runoff from irrigation and/or runoff from storm events would transport mirex residues into those lakes. Water, soil, and mosquitofish samples were analyzed from the lakes and the results are presented in Figure 6. The amount of mirex in the water and fish disappeared rapidly during the late summer and early fall. The residues in the soil, however, diminished more slowly. The concentration in all three components of this ecosystem was at least an order of magnitude lower than that observed in the golf course system. The greater volume of water and dilution from surface waters could contribute to this level of pesticide.

Another halogenated hydrocarbon pesticide was also observed on the golf course during this investigation. During August of 1974, chlordane residues were detected in samplings of water, soil, and aquatic organisms from golf course ponds and adjacent ditches (Figure 7). Of particular interest are the residues detected in crayfish from the ponds and ditches adjacent to the golf course. The highest amount of chlordane was observed in the organisms from the ponds with a lesser amount in the same organisms from the ditches. These findings appear to correlate with the amount of chlordane observed in the water samples (Figure 6). These findings suggest that the initial application may have occurred on the golf course and runoff water contributed to the residues in the ditches. During the latter part of 1975, mosquitofish and soil samples were obtained from the pond. No crayfish were present at this time. The levels of chlordane, although low, were higher than those observed in the water or soil samples. Again, it is difficult to state if this increase was due to direct adsorption or to accumulation through the food web (25,30,31).

CARBAMATE PESTICIDES

Utilizing the methodology developed by Wong and Fisher (28) and Butler and McDonough (29), an attempt was made to examine the runoff of a carbamate pesticide and its metabolites from an urban yard. Although the resemblance of a first order decay curve was observed, it was unfortunate that the first interpretation of the data was in error. Extracts of runoff waters were examined without derivatization with trifloroacetic anhydride and comparable results were obtained as with derivatized samples. During concurrent studies in a ricefield-marshland ecosystem, the same observations were made. Numerous naturally occurring compounds will effect peaks in GLC determinations, especially where electron capture is employed as the detection system. Sulfur-containing compounds are the most notorious in creating such artifacts. Samples can often be "cleaned up" by batch process or columns of bright copper or by exposing the extracted sample to mercury. The problems encountered in the determination of sevin,

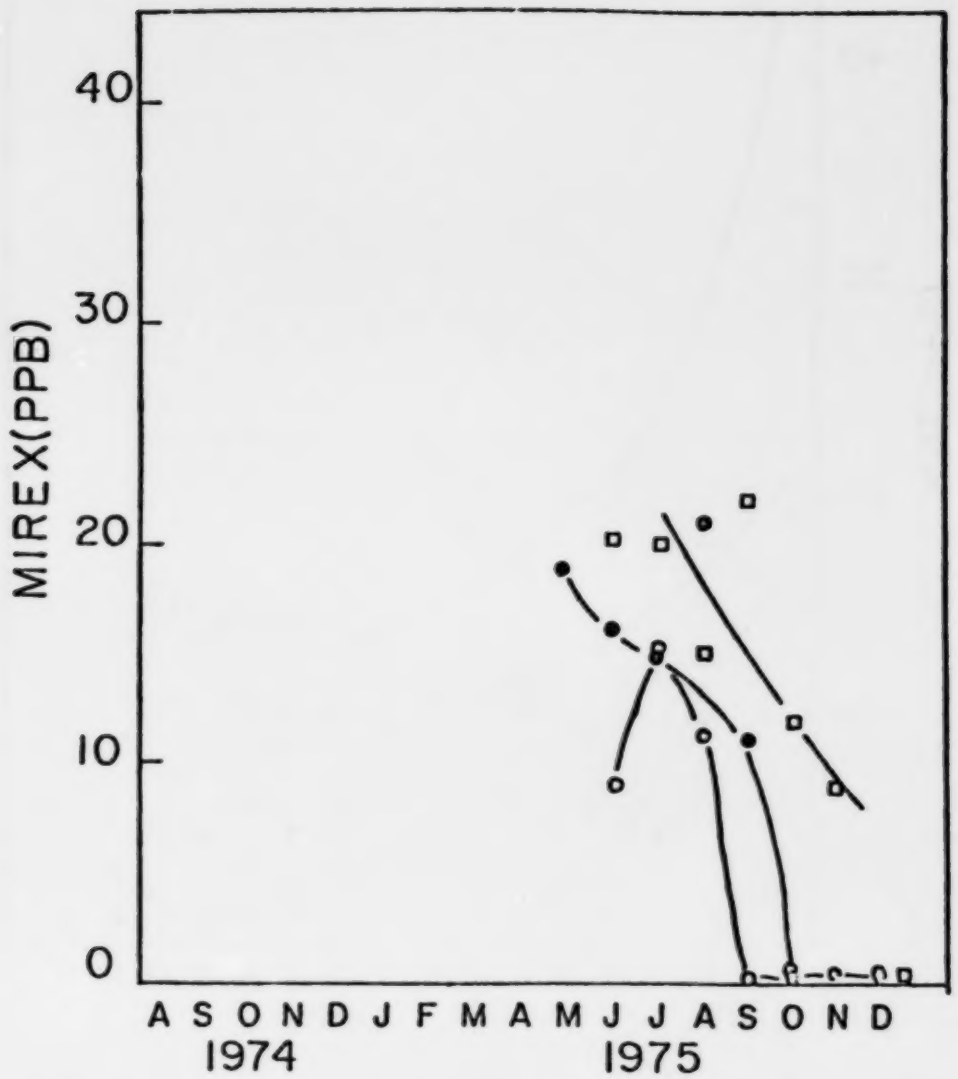

Figure 6. Temporal distribution of mirex in the Conference Center Lakes (A & B). ▫-▫ soils; ●-● mosquitofish (Gambusia sp.); o-o water.

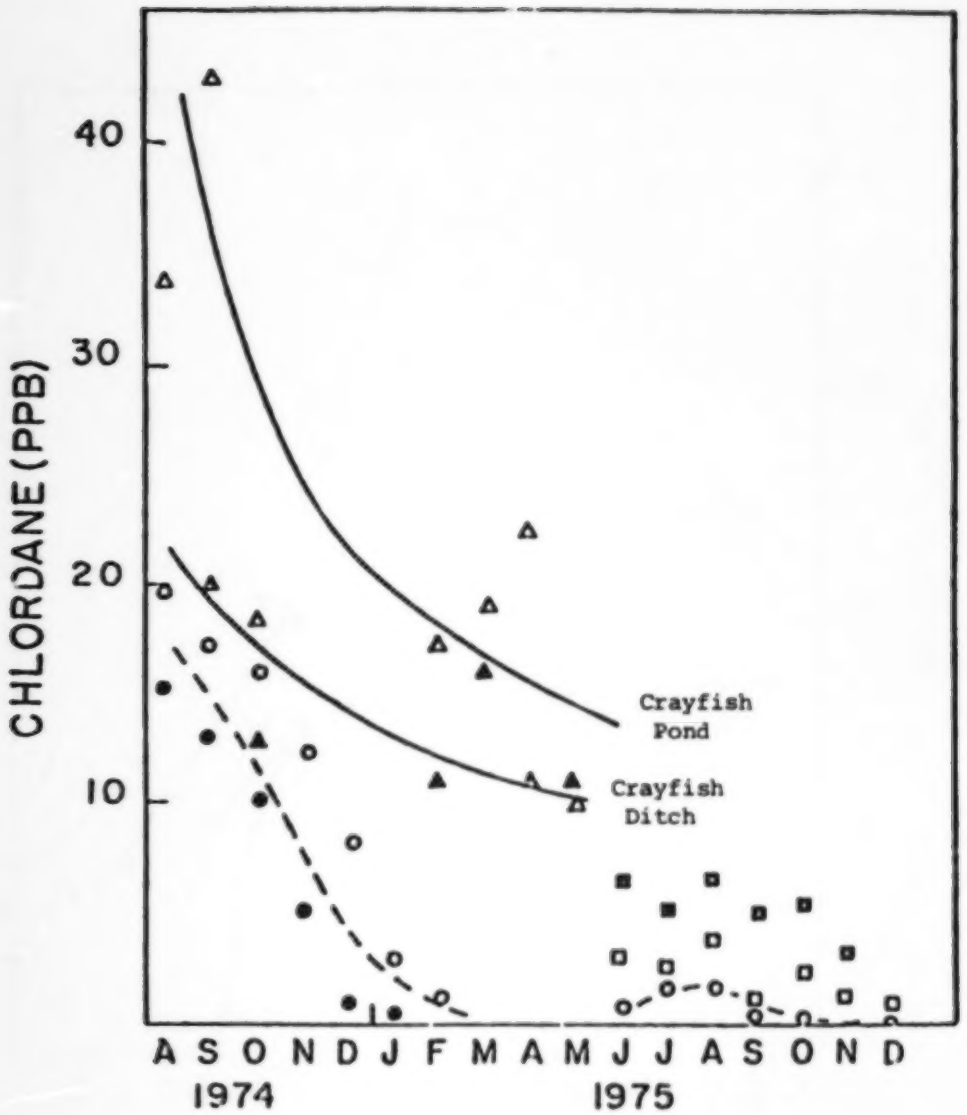

Figure 7. Temporal distribution of chlordane in The Woodlands Golf Course.
▲-▲ crayfish (Cambarus sp.) from pond;
Δ-Δ crayfish (Cambarus sp.) from ditch;
o-o pond water; ●-● ditch water; mosquitofish (Gambusia sp.) from pond; ◘-◘ soil from pond.

captan, and carbofuran are not, however, due to sulfur or sulfur compounds as treatment with copper did not reduce the peaks in the underivatized samples. With these observations, we have routinely incorporated injection of underivatized samples to preclude such future errors in analysis.

We have also observed great difficulty in determining carbamate pesticides in both standing (ricefield) or stormwaters, especially where the waters are of alkaline pH and/or high inorganic material. Further encumberances on detection are observed during periods of elevated temperature and/or intense solar radiation.

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APPENDIX A

EXPERIMENTAL PROCEDURES

GENERAL PROCEDURES

Sample Collection and Transportations

Sites for sampling water, sediments, and organisms were selected at appropriate locations along the major waterway in The Woodlands and Spring Creek, the receiving body for surface drainage from this development.

Water samples and corresponding sediment samples, as well as aquatic organisms and plants, were collected on a monthly schedule or more often during or following periods of rainfall and subsequent runoff. Biotic samples were not available during the colder winter months. Water samples were obtained by the grab method and transported in clean 3.8 l brown glass bottles with Teflon-lined caps. Sediment samples (top 7-8 cm) were collected with an aluminum scoop and wrapped in aluminum foil before enclosing in plastic bags. Animal samples were obtained with traps, seines, and nets. Biotic samples were first wrapped in aluminum foil and the foil package placed in a plastic bag. All samples, biotic and abiotic, were transported to the research laboratory in insulated chests at 0°C. Sufficient smaller organisms were collected to yield a sample of 30-120 grams. Upon receipt in the laboratory all biotic samples were stored at -20°C as were the sediment samples. Water samples were extracted 24 hours after arriving in the Houston laboratory. The resultant extracts were stored at -20°C until time for clean-up and analysis by gas-liquid chromatography (GLC).

Sample Preperation and Analytical Procedures

Samples were prepared, extracted, and processed through the preliminary "clean-up" and the GLC Analysis by the procedures outlined below.

General Comments

Glassware should be washed thoroughly in Alconox detergent or an equivalent cleaning agent and should be rinsed with tap water and glass distilled water to removed all soap residue.

The glassware should be rinsed with pesticide grade acetone prior to use.

Separatory funnels should be fitted with Teflon stopcocks and Teflon or plastic caps. With the exception of the chromatographic tubes used in the clean-up procedure, all other glassware should utilize ground-glass joints.

Solvents should be of the highest purity available to avoid the interference of electron capturing impurities. Mallinckrodt "Nanograde," Fisher "Pesticide Grade," or the equivalent purity of other manufactures should be used. Each new lot of solvents should be examined by gas-liquid chromatography prior to utilization in the analytical laboratory.

DETERMINATION OF ORGANOCHLORINE COMPOUNDS

General Comments

This procedure is essentially that of Ginn and Fisher (13).

Procedure for Animal Materials

1. A 30 gram or larger sample of animal material is admixed with Na_2SO_4 at a ratio of 1:3 in a blender jar.

2. The sample ground thoroughly to a homogenous mixture.

3. With sample in jar and cutting assembly still affixed, the jar is placed in a freezer at -20°C for 15 to 30 minutes.

4. The sample is reground and refrozen as necessary to effect a freely flowing, homogenous Na_2SO_4-tissue powder.

5. If sample is to be stored for future extraction, wrap the powder carefully in aluminum foil and affix accession number before storage in a freezer at -20°C.

6. A plug of glass wool is used in the Soxhlet to support the tissue mixture *in lieu* of paper thimbles.

7. For extraction, a weighed quantity of the tissue-Na_2SO_4 mixture is refluxed for 4 hours with 250 ml petroleum ether at a temperature sufficient to produce cycling of the solvent every 5 to 10 minutes in the Soxhlet apparatus.

8. Following the 4-hour extraction the volume of the extract is reduced to approximately 15 ml over steam using a Snyder three-ball condenser to prevent evaporative loss.

9. The reduced extract is quantitatively transferred to a separatory funnel and the volume adjusted to 50 ml with petroleum ether for partitioning over acetonitrile.

10. The extract is partitioned over a 50 ml volume of acetonitrile for one minute with vigorous agitation and frequent venting of the separatory funnel.

11. The acetonitrile is collected in an evaporating dish and step 10 repeated.

12. The combined acetonitrile extracts are reduced to near dryness on a slide warming tray at 40°C. Prolonged drying and excessive heating are to be avoided because of losses due to volatilization.

13. The resultant residue is taken up in petroleum ether and added to a 10-gram column of Florisil (Floridin Co., Berley Springs, W. Va.) contained in a 400 x 20 mm glass chromatography column.

14. The column is eluted with 150 ml of a 6% solution of anhydrous ether in petroleum ether. The eluate being collected in a flask with ground glass neck.

15. The column is next eluted with 150 ml of a 15% solution of ethyl ether in petroleum ether. This eluate being collected in glassware as in step 14.

16. The 6% eluate from step 14 is reduced to approximately 15 ml by evaporation over steam with a Snyder three-ball condenser affixed to the flask.

17. The reduced 6% eluate is quantitatively transferred to a glass-stoppered graduate cylinder and the volume adjusted to 25 ml with petroleum ether. This fraction is suitable for GLC analysis without further manipulation.

18. The 15% eluate is reduced to approximately 20 ml over steam and quantitatively transferred to a 400 x 20 mm chromotographic tube charged with 10 g of a 1:1 (w/w) mixture of magnesium oxide and "Celite" (Johns Manville Co.).

19. The column is eluted with 100 ml petroleum ether under a vacuum sufficient to effect a flow of about 35 ml per minute.

20. The eluate is reduced over steam quantitatively transferred to a glass-stoppered graduate cylinder and the volume adjusted to a known volume with petroleum ether prior to analysis by GLC.

Procedure for Plant Materials

1. Plant materials to be extracted are reduced in size by the use of a food chopper, food cutter, or knife.

2. The reduced material is placed in a Mason jar affixed with a cutting assembly and ground with 1 ml acetronitrile/gram/ plant material and ground at high speed for 5 minutes.

3. The homogenate is allowed to settle in the grinding jar and the supernatant acetonitrile decanted into a crystallizing dish.

4. Fresh acetonitrile (same ratio) is added and the material reground for 5 minutes at high speed.

5. The combined extracts are evaporated to dryness on a slide warming tray at 40°C.

6. The soil is discarded and the extract evaporated to dryness on a slide warmer at 40°C.

7. The residue is resuspended in petroleum ether and subjected to preparative chromatography in Florisil as above (step 13).

Procedure for Water and Soil

1. A 2000 ml or larger water sample or 100 gram or larger sample of soil is extracted in separatory funnels by agitation for 5 minutes with 100-150 ml of hexane. Occasionally two original field samples are extracted and the extracts combined (step 4).

2. The phases are allowed to separate and the solvent collected in an Erlenmeyer flask over anhydrous Na_2SO_4.

3. The sample is extracted a second and third time with equivalent volumes of solvent.

4. The combined extracts are dehydrated with anhydrous Na_2SO_4 and the supernatant poured into clean flask ground glass neck flask.

5. The Na_2SO_4 is washed with petroleum ether and added to the extracts.

6. The volume of the extract is reduced to approximately 15 ml over steam with a Snyder three-ball condenser affixed to the flask.

7. The extract is adjusted to a known volume in a glass-stoppered graduate cylinder and subjected to GLC analysis or

8. The extract is subjected to preparative chromatography as above.

NOTE: Numerous stormwater and wastewater samples, especially urban, industrial, or developing areas, have many substances which interfere with GLC analysis utilizing the electron capture method of detection. Treatment of extracts from step 7 above with bright copper or mercury often removes the interfering substances. Passage of 1 ml of the extract over a 2 cm bed of bright copper in a 20 x 1 cm chromatographic column is the most efficient clean-up procedure.

Analytical Instrumentation

1. Residue analysis is by gas-liquid chromatography on a Varian Aerograph Model 2100 dual channel chromatograph equipped with tritium electron detection detectors.

2. Read out is on a Varian Aerograph Model 20 dual Ren recorder.

3. On-column injection into an all-glass system is incorporated to prevent decomposition of certain organochlorine compounds (27).

4. Columns are 180 cm capillary U-tubes with 2 mm internal deameter.

5. Packing material consists of 80/100 mesh Gas Chrom Q (Applied Sci. Lab.) solid phase with silicone oil liquid phases.

6. Liquid phases are 3% DC-200, 5% QF-1, a 2:1 mixture of 5% QF-1 and 5% DC-200 as well as a 3:1 mixture of 3% DC-200 and 10% OV-17.

7. Nitrogen is used as the carrier gas at 65 psi and rate of flow of 40 ml/m.

8. The column temperature is 190°C.

9. The injection is at 215°C to insure rapid and complete volatilization.

10. Sufficient sensitivity is achieved without exceeding the thermal limit for Tritium dectectors (225°C by operating the detector at 215°C).

11. Maintaining detector temperature above that of the columns prevents condensation of sample in the detectors and negates loss of sensitivity and frequent cleaning of the detector foils.

12. The detectors operate on a 90 volt DC mode.

13. Though this range of electron capture detectors is limited, linearity is obtained in the range of pesticide concentration assayed (10^{-11} to 10^{-9}).

14. Data are quantitated by comparison of printout of sample peak height and/or area with comparable standard mixture pesticides.

15. Standards are injected following every third experimental sample.

16. Confirmation of analysis is achieved by use of two liquid phases of differing polarity such as DC-200 and QF-1.

17. Additional confirmation is gained by the use of binary solvent systems which rely on the solubility ratios of pesticides in immiscible solvents.

DETERMINATION OF CARBAMATE PESTICIDES

General Comments

This procedure is a modification of the procedure presented by Wong and Fisher (28).

Procedure for Animal Materials

1. Place 30 grams of animal material in a quart blending jar, add 200 ml anhydrous methanol, and fit the jar with a cutting assembly. Blend the sample completely.

2. Filter the methanolic extract through a large funnel containing anhydrous sodium sulfate and collect the cleared extract in a 850 ml beaker. Rinse the insoluble material on the sodium sulfate filter with 300 ml methanol. Combine the rinse with the initial methanol extract.

3. Place the beaker under a light stream of air on a steam table and evaporate the methanol extract to near dryness.

4. Redissolve the residue in 500 ml 0.25 N HCl and transfer the aqueous mixture to a 1000 ml round bottom boiling flask. Add several boiling chips to the flask, connect an Allihn condenser, and set the flask in an electric heating mantle. Reflux the mixture for 1 hour.

5. Disconnect the Allihn condenser and chill the flask in an ice bath. Transfer the sample to a 1000 ml separatory funnel. Rinse the round bottom flask with 50 ml glass distilled water and transfer the rinse to the separatory funnel.

6. Add 100 ml methylene chloride and extract the aqueous phase by shaking the separatory funnel vigorously for 1 minute. Allow the phases to separate, then drain the methylene chloride phase (lower phase) into a 500 ml evaporating flask through a funnel containing anhydrous sodium sulfate. Repeat the extraction of the aqueous phase with two 100 ml volumes of methylene chloride. Combine the extractions and rinse the sodium sulfate funnel with 50 ml methylene chloride.

7. Add boiling sand to the flask, connect a Snyder column, and evaporate the solvent to approximately 50 ml on a steam table.

8. First Activated Florisil Column Clean-up: Prepare a 400 x 20 mm chromatographic tube with 12.5 cm of activated Florisil topped with 2.5 cm anhydrous sodium sulfate. (The Florisil is activated by heating at 135°C for a minimum of 24 hours.) Attach the column to a vacuum flask and add the concentrated methylene chloride extract in 1 to 2 ml aliquots, at intervals, to permit the complete evaporation of solvent and the collection of residue on the top 2.5 to 5 cm of the Florisil column. Rinse the flask with three 5 ml volumes of methylene chloride and add each rinse to the column in small aliquots as described above.

9. Disconnect the column from the vacuum flask and elute the column with 300 ml 35% ethyl acetate in hexane (v/v). Collect the eluate in a 500 ml flask. Add boiling sand to the flask, fit the flask with a Snyder column, and evaporate the solvent to approximately 5 ml on a steam table. Add 50 ml of petroleum ether to the flask and reduce the volume to 5 ml on the steam table.

10. Clean-up by Solvent Partition: Transfer the petroleum ether sample to a 250 ml separatory funnel, along with two 10 ml petroleum ether rinses of the flask. Rinse the flask with two 50 ml volumes of a 9:1 mixture of acetonitrile-water and transfer both rinses to the separatory funnel. Vigorously shake the separatory funnel for 2 minutes to partition the carbamate residues into the acetonitrile-water phase.

11. Allow the phases to separate, then drain the lower phase (acetonitrile-water) into a second 250 ml separatory funnel. Extract the acetonitrile-water sample with two additional 20 ml volumes of petroleum ether and discard both petroleum ether fractions.

12. Drain the acetonitrile-water phase into a crystallizing dish, along with two 10 ml acetonitrile-water rinses of the separatory funnel. Place the crystallizing dish on a slide warming tray (45°C) and allow the complete evaporation of the solvent.

13. Second Activated Florisil Clean-up: Prepare a 400 x 20 cm chromatographic tube with 12.5 cm of activated Florisil and top the activated Florisil column with 1.25 cm of anhydrous sodium sulfate. Prewet the column with approximately 50 ml of hexane.

14. Redissolve the acetonitrile-water residue in 1 ml ethyl acetate or less, and dilute with 5 ml hexane. Transfer the sample to the column along with three 10 ml 6% ethyl acetate in hexane rinses of the crystallizing dish. Elute with 300 ml 6% EA, acetonitrile and hexane and discard.

15. Elute the column with 300 ml of hexane containing 1% acetonitrile and 15% ethyl acetate (v/v) and collect the eluate in a 500 ml evaporating flask. This solvent mixture elutes carbofuran and 3-ketocarbofuran from the column.

16. Elute the column with 300 ml of 35% ethyl acetate in hexane to recover 3-hydroxycarbofuran. Collect the eluate in a second 500 ml evaporating flask.

17. Add boiling sand to each flask and attach a Snyder column. Place the flask on a steam table and evaporate the solvent to approximately 50 ml. Transfer the sample to a crystallizing dish, along with two 10 ml ethylacetate-hexane rinses of the flask and evaporate the samples to dryness on a slide warming tray (45°C).

18. Remove the crystallizing dishes from the slide warming tray when the last of the solvent has evaporated, then redissolve the residue in 2.0 ml (or other known volume) ethyl acetate. Transfer the ethyl acetate sample to 2-dram vials sealed with Teflon-lined caps.

19. Prepare the N-trifluoroacetyl derivatives of carbofuran, 3-hydroxycarbofuran, and 3-ketocarbofuran according to the procedure described in the section on water analysis. The gas-liquid chromatography of the derivatives is also as described.

Procedure for Water

1. Transfer 1500 ml of water (acidified to 0.25 N HCl) to a 200 ml round bottom flask and add several boiling chips. Connect an Allihn condenser to the flask and set the flask in an electric heating mantle. Reflux the water for 1 hour.

2. Disconnect the Allihn condenser and chill the flask in an ice bath. Transfer the water to a 2000 ml separatory funnel (Teflon stopcock and Teflon or plastic stopper). Rinse the round bottom flask with 50 ml glass distilled water and transfer the rinse to the separatory funnel.

3. Add 100 ml of methylene chloride to the separatory funnel and extract the aqueous phase by shaking the separatory funnel vigorously for 1 minute. Allow the two phases to separate and drain the methylene chloride phase (lower phase) into a 500 ml evaporating flask, through a funnel containing anhydrous sodium sulfate. Extract the aqueous phase with two additional 100 ml of methylene chloride. Rinse the funnel of sodium sulfate with 50 ml methylene chloride.

4. Add boiling sand to the flask and attach a Snyder column. Place the flask on a steam table and evaporate the methylene chloride to approximately 5 ml. Add 50 ml of petroleum ether to the flask through the column and evaporate the solvent mixture to approximately 5 ml on the steam table.

5. Prepare a 400 x 20 mm chromatographic tube (Kontes) with 12.5 cm of activated Florisil and top the Florisil bed with 2.5 cm of anhydrous sodium sulfate. (Activate the Florisil by heating at 135°C for a minimum of 24 hours.) Prewet the column by adding 50 ml (petroleum ether) hexane.

6. Transfer the petroleum ether-water extract to the column along with two 10 ml hexane:acetonitrile:ethyl acetate (84:1:15) rinses of the flask. Elute the column with 300 ml of the same hexane:acetonitrile:ethyl acetate mixture and collect the eluate in a 500 ml evaporating flask. This solvent mixture elutes carbofuran and 3-ketocarbofuran selectively from the column.

7. Elute the column with 300 ml 35% ethyl acetate in hexane and collect the eluate in a second 500 ml evaporating flask. This solvent mixture elutes 3-hydroxycarbofuran.

8. Add boiling sand to each flask and attach a Snyder column. Evaporate the solvent mixtures to approximately 50 ml on a steam table. Rinse the Synder column with several ml of hexane, then disconnect. Transfer the concentrated eluates to crystallizing dishes and place the crystallizing dishes on a slide warming tray (45°C) to evaporate the remaining solvent.

9. Remove the crystallizing dishes from the slide warming tray when the last of the solvent has evaporated. Allow the crystallizing dishes to cool to room temperature, then redissolve the residue in 2.0 ml of ethyl acetate. Transfer the ethyl acetate sample to a 2-dram vial with Teflon-lined caps.

10. Carbofuran, 3-hydroxycarbofuran, and 3-ketocarbofuran are prepared for gas-liquid chromatography as N-trifluoroacetyl derivatives according to the following procedure:

a. Transfer 0.2 ml of the ethyl acetate sample to a second 2-dram vial.

b. Carefully pipet 0.1 ml of trifluoroacetic anhydride (Aldrich Chemical Co.) to the vial and seal the vial tightly with a Teflon-lined cap.

c. Wrap the vial in aluminum foil to protect from light and place the vial on a slide warming tray (45°C) for a minimum of 16 hours for the complete derivatization.

d. At the completion of the reaction, remove the vial from the slide warming tray and allow the vial and its contents to come to room temperature. Open the vial and add 2 ml hexane and 4 ml of glass distilled water. Reseal the vial and shake the vial vigorously to destroy the unreacted trifluoroacetic anhydride. Allow the phases to separate, then with a Pasteur pipet remove the aqueous phase (lower phase) and discard this phase. Wash the hexane phase with two additional 4 ml volumes of glass distilled water.

e. Transfer the hexane phase to a 25 ml graduated cylinder through a small funnel containing anhydrous sodium sulfate. Rinse the vial with three 2 ml volumes of hexane and transfer each rinse to the graduated cylinder. Rinse the sodium sulfate with 5 ml hexane.

f. Record the final volume of the hexane sample and gas-liquid chromatograph at 5 µl aliquot.

11. Prepare fresh derivatized standards of carbofuran, 3-hydroxycarbofuran, and 3-ketocarbofuran for each group of samples analyzed. Convenient stock standard solutions are 100 µg/ml carbofuran, 10 µg/ml 3-ketocarbofuran, and 5 µg/ml 3-hydroxycarbofuran, in ethyl acetate. Derivatize 0.2 ml of each stock standard as described above with 0.1 ml trifluoroacetic anhydride in a 2-dram vial sealed with a Teflon-lined cap.

12. Gas-liquid Chromatography: A Varian Aerograph Model 2100 is equipped with two 6-ft glass columns (2 mm i.d.) and tritium foil electron capture detectors. Column one is packed with 3% DC-200 on Gas Chrom Q, 30/100 mesh. The columns are maintained at 175°C, injected port at 220°C, and detectors at

215°C. Gas flow (Zero grade N_2) is 60 ml/min and the recorder is a dual pen Varian Model 20.

13. Identify carbofuran and its carbamate metabolites by comparison of peak retention times on the two columns.

14. Calculate residue concentration on the basis of peak height and/or area.

DETERMINATION OF CARBAMATE PHENOLS

General Comments

This procedure is a modification of a procedure presented by Wong and Fisher (28). The procedure for the trichloroacetylation of the phenols is basically that of Butler and McDonough (29).

Procedure for Water

1. Transfer 1500 ml of water (acidified to 0.25 N HCl) to a 2000 ml round bottom flask and add several boiling chips. Connect an Allihn condenser to the flask and set the flask in an electric heating mantle. Reflux the water for 1 hour.

2. Disconnect the Allihn condenser and chill the flask in an ice bath. Transfer the water to a 2000 ml separatory funnel along with a 50 ml glass distilled water rinse of the round bottom flask.

3. Add 100 ml of methylene chloride to the separatory funnel and extract the aqueous phase by shaking the separatory funnel vigorously for 1 minute. Allow the two phases to separate and drain the methylene chloride (lower phase) into a 500 ml evaporating flask, through a funnel containing anhydrous sodium sulfate. Extract the aqueous phase with two additional 100 ml methylene chloride. Rinse the funnel of sodium sulfate with 50 ml methylene chloride.

4. Add boiling sand to the flask and attach a Synder column. Place the flask on a steam table and evaporate the methylene chloride to approximately 5 ml. Add 50 ml of petroleum ether through the column to the flask and evaporate the solvent mixture to approximately 5 ml on the steam table.

5. Prepare a 400 x 20 mm chromatographic tube (Kontes) with 12.5 cm of activated Florisil and top the Florisil bed with 2.5 cm of anhydrous sodium sulfate. (Activate the Florisil by heating at 135°C for a minimum of 24 hours.) Prewet the column by adding 50 ml (petroleum ether) hexane.

6. Transfer the petroleum ether-water extract to the column along with two 10 ml 35% ethylacetate in hexane rinses of the

flask. Elute the column with 400 ml of the same solvent mixture and collect the eluate in a 500 ml evaporating flask.

7. Add boiling sand to the flask and attach a Synder column. Evaporate the solvent mixture to approximately 50 ml on a steam table. Rinse the Synder column with several ml of hexane, then disconnect. Transfer the sample to a crystallizing dish on a slide warming tray (45°C) to evaporate the remaining solvent.

8. Remove the crystallizing dish from the slide warming tray when the last of the solvent has evaporated. Allow the crystallizing dish to cool to room temperature then redissolve the residue in 2.0 ml (or other known volume) ethyl acetate. Transfer the ethyl acetate sample to a 2-dram vial with a Teflon-lined cap.

9. Carbofuran phenol, 3-hydroxycarbofuran phenol, and 3-ketocarbofuran phenol are prepared for gas-liquid chromatography as N-trichloroacetyl derivatives according to the following procedure:

a. Transfer 0.2 ml of the ethyl acetate sample to a second 2-gram vial and under a light stream of N_2 evaporate the ethyl acetate solvent.

b. Add 1 ml pyridine solution (0.1 ml Florisil eluted pyridine in 99.9 ml methylene chloride, stored in a dark bottle) and heat vial on a steam table (90-100°C) until the methylene chloride is evaporated.

c. Cool the vial to room temperature, then add 1 ml trichloroacetyl chloride solution (0.1 ml trichloroacetyle chloride in 9.9 ml methylene chloride). Heat the vial on a steam table (90-100°C) until the methylene chloride is evaporated (3 to 5 minutes).

d. Remove the vial from the steam table and add 2 ml hexane and 4 ml saturated sodium bicarbonate solution. Seal the vial with a Teflon-lined cap and shake vigorously to destroy the unreacted trichloroacetyl chloride.

e. Allow the phases to separate. With a Pasteur pipet withdraw the aqueous phase (lower phase) and discard. Wash the hexane phase by extracting twice with 4 ml volumes of glass distilled water. Discard each wash.

f. Transfer the hexane phase to a 25 ml graduated cylinder through a small anhydrous sodium sulfate funnel. Rinse the vial with two ml volumes of

hexane. Rinse the sodium sulfate funnel with 5 ml hexane.

g. Record the volume of the hexane sample and gas-liquid chromatograph a 5 µl aliquot.

Quality Control

Routinely blank samples were processed to examine for possible interfering substances in analytical materials and reagents. Standard solutions were prepared in appropriate solvents using analytical grade compounds obtained from the Pesticide Repository, Perrine, Florida. Duplicate injections of experimental samples and standard solutions were routinely examined. Quantitation of data was determined by comparison of printout of sample extract peak with the peaks from standard solutions. Although the linear range of electron-capture detectors is limited, linearity was obtained in the range of concentration examined (10^{-11} to 10^{-9} g). Peak height and/or area was used to estimate sample concentration. Samples corresponding to the collected environmental samples were routinely spiked with relevant compounds to examine recovery efficiency. Chlorinated hydrocarbon compound recovery was always above 95%.

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TABLE 1. SURVEY OF POLYCHLORINATED BIPHENYLS IN UPPER BEAR BRANCH AT B-04 (9/1/73 to 6/30/74)

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	ppb 1	2	3	Animal	ppb 1	2	3
S	5	-	1	4	4	-	1	3	2	-	-	2	2	-	-	2
O	2	-	1	1	2	-	1	1	0				5	-	1	4
N	5	-	2	3	0				1	-	-	1	4	-	-	4
D	0				0				0				0			
J	3	-	1	2	2	-	1	1	0				0			
F	8	1(1.9)	2	5	2	-	1	1	0				0			
M	5	-	2	3	0				2	-	-	2	6	-	3	3
A	6	1(1.2)	2	3	2	-	2	-	1	-	-	1	2	-	-	2
M	2	0	1	1	2	-	1	1	2	-	-	2	4	-	-	4
J	0				0				0				1	-	-	1

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 2. SURVEY OF POLYCHLORINATED BIPHENYLS IN UPPER PANTHER BRANCH AT P-04 (9/1/73 to 6/30/74)

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	ppb 1	2	3	Animal	ppb 1	2	3
S	15	-	9	6	4	-	2	2	4	-	-	4	10	-	1	9
O	8	1(1.1)	2	5	4	-	4	-	2	-	-	2	12	2(1.3)	2	8
N	7	1(1.0)	2	4	2	-	2	-	1	-	-	1	8	-	2	6
D	3	-	2	1	7	3(73.0)	4	-	1	-	-	1	2	-	2	-
J	5	-	2	3	2	1(80.0)	-	1	0				2	-	1	1
F	8	2(1.2)	3	3	2	1(90.2)	1	-	0				4	1(130)	2	1
M	5	-	2	3	2	1(97.0)	1	-	3	-	1	2	11	4(120)	6	1
A	14	3(1.2)	6	5	2	1(83.0)	1	-	1	-	-	1	5	2(250)	3	-
M	8	-	3	5	5	2(92.0)	2	1	2	-	-	2	12	3(130)	8	1
J	4	1(1.0)	1	2	1	-	1	-	0				3	1(100)	2	-

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 3. SURVEY OF POLYCHLORINATED BIPHENYLS AT SITE P-20 ON PANTHER BRANCH (9/1/73 to 6/30/74)

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	ppb 1	2	3	Animal	ppb 1	2	3
S	9	-	4	5	0				2	-	-	2	5	-	-	5
O	10	-	6	4	4	-	2	2	0				8	-	4	4
N	0				0				0				12	-	3	9
D	0				0				1	-	-	1	3	-	-	3
J	2	-	1	1	2	-	2	-	0				0			
F	5	2(1.6)	1	2	2	1(80)	1	-	0				2	-	2	-
M	5	3(2.1)	1	1	2	2(130)	-	-	2	-	-	2	10	3(7.0)	6	1
A	10	6(2.3)	4	-	2	2(172)	-	-	1	-	-	1	5	-	5	-
M	4	2(1.4)	2	-	2	1(30)	1	-	2	-	1	1	3	-	2	1
J	1	1(1.4)	-	-	0				0				5	-	3	2

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 4. SURVEY OF POLYCHLORINATED BIPHENYLS AT SITE P-30 ON PANTHER BRANCH (9/1/73 to 6/30/74)

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	ppb 1	2	3	Animal	ppb 1	2	3
S	21	1(1.2)	16	4	4	-	3	1	2	-	-	2	5	-	-	5
O	15	1(1.3)	11	3	2	-	1	1	2	-	-	2	6	-	1	5
N	7	-	5	2	2	-	1	1	1	-	-	1	10	-	2	8
D	15	3(1.1)	6	6	4	1(51)	2	1	1	-	-	1	3	-	1	2
J	3	1(1.0)	2	-	2	-	2	-	0				1	-	1	-
F	10	5(3.6)	3	2	2	2(341)	-	-	0				2	-	2	-
M	5	5(1.5)	-	-	2	2(200)	-	-	2	-	1	1	5	2(4.6)	2	1
A	13	1(4.8)	1	11	2	2(54)	-	-	1	-	-	1	8	2(3.5)	6	-
M	6	2(1.1)	2	2	2	-	2	-	2	-	1	1	2	2(1.1)	-	-
J	4	3(3.4)	-	1	3	-	3	-	0				3	-.	3	-

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 5. SURVEY OF POLYCHLORINATED BIPHENYLS AT SITE S-10 ON SPRING CREEK AT

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	ppb 1	2	3	Animal	ppb 1	2	3
S	11	-	2	9	4	-	-	4	2	-	-	2	5	-	-	5
O	15	-	7	8	3	-	1	2	2	-	-	2	8	-	-	8
N	11	1(1.1)	3	7	2	-	-	2	2	-	-	2	6	-	1	5
D	15	3(1.2)	6	6	4	1(10)	2	1	2	-	-	2	5	-	1	4
J	3	-	1	2	2	-	2	-	0				2	-	-	2
F	12	-	5	7	2	-	2	-	0				2	-	1	1
M	10	1(1.1)	4	5	2	-	2	-	2	-	-	2	10	3(1.7)	5	2
A	10	2(1.2)	5	3	2	1(4.0)	-	1	1	-	1	-	3	1(1.3)	-	2
M	10	2(1.1)	3	5	4	-	3	1	2	-	1	1	8	4(1.0)	-	4
J	2	-	1	1	3	-	1	2	0				8	1(1.3)	6	1

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 6. SURVEY OF POLYCHLORINATED BIPHENYLS IN LAKE A (9/1/73 to 6/30/76)

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	Animal	ppb 1	2	3
S	6	-	4	2	5	0	1	4	0	6	-	2	4
O	1	-	-	1	2	-	-	2	0	5	-	2	3
N	7	1(1.9)	3	3	4	1(1.0)	-	3	0	5	1(1.7)	4	-
D	11	2(2.0)	7	2	4	1(1.0)	-	3	0	2	2(3.2)	-	-
J	4	1(2.1)	2	1	4	-	4	-	0	2	-	2	-
F	10	-	3	7	2	1(92)	1	-	0	2	2(4.3)	-	-
M	15	4(8.2)	5	6	2	1(239)	1	-	0	1	1(62.0)	-	-
A	8	4(6.1)	3	1	2	2(170)	-	-	0	2	2(37.0)	-	-
M	5	1(1.0)	1	3	4	2(120)	1	1	0	3	3(15.7)	-	-
J	0				2	-	2	-	0	0			

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 7. SURVEY OF POLYCHLORINATED BIPHENYLS IN LAKE B (9/1/73 to 6/30/74)

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	Animal	ppb 1	2	3
S	0				4	-	3	1	0	0			
O	0				2	-	2	-	0				
N	3	-	1	2	4	-	3	1	0				
D	8	1(2.0)	3	4	4	1(13.0)	2	1	0	0			
J	2	-	1	1	2	-	2	-	0	1	-	1	-
F	6	-	3	3	0				0	2	-	2	-
M	8	3(2.5)	4	1	0				0	0			
A	10	4(2.1)	3	3	2	1(161)	1	-	0	1	1(36.0)	-	-
M	3	1(1.1)	1	1	2	1(173)	1	-	0	2	2(49.1)	-	-
J	2	-	1	1	3	2(130)	1	-	0	0			

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 8. SURVEY OF POLYCHLORINATED BIPHENYLS IN THE CONFERENCE CENTER MARSH (CCM) (9/1/73 to 6/30/74)

Month	Water	ppb 1	2	3	Soil	ppb 1	2	3	Plant	ppb 1	2	3	Animal	ppb 1	2	3
S	6	2(1.0)	2	2	4	-	-	4	4	-	-	4	10	3(6.0)	1	6
O	0				4	-	-	4	4	-	-	4	6	-	6	-
N	9	4(1.3)	3	2	2	-	-	2	0				13	3(61)	7	3
D	11	2(1.2)	7	2	3	-	2	1	2	-	-	2	0			
J	2	-	1	1	3	1(3.1)	1	1	0				4	2(16)	2	-
F	5	3(2.1)	2	0	0				0				2	1(130)	1	-
M	7	-	4	3	1	1(16)	-	-	3	-	1	2	17	5(300)	10	2
A	3	-	2	1	2	-	-	2	0				12	5(230)	5	2
M	5	1(2.0)	2	2	1	-	-	1	5	-	-	5	22	11(112)	7	4
J	2	1(1.2)	1	-	0				1	-	-	1	5	2(32)	3	-

1 Quantifiable level

2 Trace levels

3 Not detectable

Numbers indicate number of samples; positive samples are followed by average amount in parenthesis.

TABLE 9. RESUME OF DISTRIBUTION OF POLYCHLORINATED BIPHENYL RESIDUES FROM THE WOODLANDS (9/1/73 to 6/30/74)

Study Sites	Measurable Levels				Trace Levels				Not Detectable			
	HOH	Soil	Plant	Animal	HOH	Soil	Plant	Animal	HOH	Soil	Plant	Animal
B-04	2	0	0	0	12	7	0	4	22	7	8	20
P-04	8	9	0	13	32	18	1	29	31	4	13	27
P-20	14	6	0	3	23	6	1	28	12	2	7	22
P-30	22	7	0	5	46	14	2	19	31	4	9	21
S-10	9	2	0	7	37	13	2	15	53	13	11	34
Lake A	13	6	0	11	25	12	0	10	26	13	0	7
Lake B	9	5	0	3	17	15	0	3	16	3	0	0
Conference Center Marsh	13	2	0	32	24	3	1	42	13	15	18	17

TABLE 10. POLYCHLORINATED BIPHENYL DISTRIBUTION IN ANIMALS
(9/1/73 to 6/30/74)

	B-04			P-04			P-20			P-30		
Month	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
S	2	0	0	10	1	10	5	0	0	5	0	0
O	5	1	20	12	4	12	8	4	50	6	1	17
N	4	0	0	8	2	25	12	3	25	10	2	20
D	-	-	-	2	2	100	3	0	0	3	1	33
J	-	-	-	2	1	50	-	-	-	2	1	50
F	-	-	-	4	3	75	2	2	100	2	2	100
M	6	3	50	10	10	100	10	9	90	5	4	80
A	2	0	0	5	5	100	5	5	100	8	8	100
M	4	0	0	12	11	92	3	2	66	2	2	100
J	1	0	0	3	3	100	5	3	60	3	3	100
Total	24	4	17	68	42	62	45	28	62	37	24	65

(1) Total number analyzed

(2) Total positive, including samples with trace amounts

(3) % positive samples

TABLE 10. (Continued)
POLYCHLORINATED BIPHENYL DISTRIBUTION IN ANIMALS
(9/1/73 to 6/30/74)

Month	S-10			Lake A			Lake B			CCM		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
S	5	0	0	6	2	33	-	-	-	10	1	10
O	8	0	0	5	2	40	2	0	0	6	6	100
N	6	1	17	5	5	100	1	0	0	13	7	54
D	5	1	20	2	2	100	-	-	-	-	-	-
J	2	0	0	2	2	100	1	1	100	4	4	100
F	2	1	50	2	2	100	2	2	100	2	2	100
M	10	8	80	1	1	100	-	-	-	17	15	88
A	3	1	33	2	2	100	1	1	100	12	10	83
M	8	4	50	3	3	100	2	2	100	22	18	82
J	8	6	75	-	-	-	-	-	-	5	5	100
Total	60	22	37	28	21	75	9	6	67	71	68	96

(1) Total number analyzed

(2) Total positive, including samples with trace amounts

(3) % positive samples

TABLE 11. SPECIES DISTRIBUTION OF POLYCHLORINATED BIPHENYLS
(9/1/73 to 6/30/74)

Month	B-04					P-04					P-20					P-30				
	(1)	(2)	(3)	(4)	T	(1)	(2)	(3)	(4)	T	(1)	(2)	(3)	(4)	T	(1)	(2)	(3)	(4)	T
S	-	-	-		1	-	-	-	1	1										
O				1		-	1	1	2	4	-	1	-	3	4	-	-	-	1	1
N						-	-	-	2	2	-	-	1	2	3	-	-	-	2	2
D						-	-	-	2	2						-	-	-	1	1
J						-	-	-	1	1						-	-	-	1	1
F						-	-	1	2	3	-	1	-	1	2	-	1	-	1	2
M	-	-	-	3	3	1	3	2	4	10	1	-	3	6	9	-	2	-	2	4
A						-	-	2	3	5	-	1	1	3	5	-	2	3	3	8
M						-	3		8	11	-	1		1	3	-	-	-	2	2
J						1	-	-	2	3	-	-	2	1	2	-	1	-	2	3
Totals	-	-	-	4	4	2	7	6	27	42	1	4	7	17	28	0	6	3	15	24

(1) Grass shrimp (Palaemonetes sp.)

(2) Bluegill (Lepomis sp.)

(3) Crayfish (Cambarus sp.)

(4) Mosquitofish (Gambusia sp.)

T = Total samples

TABLE 11. (Continued) SPECIES DISTRIBUTION OF POLYCHLORINATED BIPHENYLS
(9/1/73 to 6/30/74)

Month	S-10					Lake A					Lake B					CCM				
	(1)	(2)	(3)	(4)	T	(1)	(2)	(3)	(4)	T	(1)	(2)	(3)	(4)	T	(1)	(2)	(3)	(4)	T
S						-	-	-	2	2						-	1	-	3	4
O						-	-	-	2	2						-	-	1	5	6
N	-	-	-	1	1	-	1	-	4	5						-	-	3	7	10
D	-	-	-	1	1	-	-	-	2	2										
J						-	-	-	2	2	-	-	-	1	1	-	2	-	2	4
F	-	-	-	1	1	-	-	-	2	2	-	-	-	2	2	-	1	-	1	2
M	-	3	-	5	8	-	-	-	1	1						-	5	4	6	15
A	-	-	-	1	1	-	-	-	2	2	-	-	-	1	1	-	5	-	5	10
M	-		-	4	4	-		-	3	3	-	-	-	2	2	-	3	4	11	18
J	-	3	1	3	7											-	3	-	2	5
Totals	0	6	1	16	23	0	1	0	20	21	-	-	-	6	6	-	20	12	42	74

(1) Grass shrimp (*Palaemonetes* sp.)

(2) Bluegill (*Lepomis* sp.)

(3) Crayfish (*Cambarus* sp.)

(4) Mosquitofish (*Gambusia* sp.)

T = Total samples

TABLE 12. DISTRIBUTION OF TRACE AMOUNTS OF DDE IN ANIMALS
(9/1/73 to 6/30/74)

Month	P-04	Lake A	P-30	S-10	CCM
S		2[1]			
O	1[1]	2[1]	1[1]		
N		1[1]	2[1]		
D	1[1]		1[1]		
J					
F			1[2]		
M	2[1], 1[2]	1[1]	2[1], 2[2]	3[2]	
A		2[1]	2[1], 1[2]		
M	1[1]	1[1]	2[1]	1[2]	1[1]
J				1[2]	1[1]
Totals	5[1], 1[2]	9[1]	10[1], 4[2]	5[2]	2[1]

[1]Mosquitofish (Gambusia sp.)

[2]Crayfish (Cambarus sp.)

TABLE 13. DISTRIBUTION OF DIELDRIN IN ANIMALS
(9/1/73 to 6/30/74)

Month	P-04	P-30	Lake A
S			1[1] (11.3)
O			
N			
D			1[1]
J			
F			
M	1[2]	1[3]	
A		2[1]	2[1]
M			1[1] (1.3)
J		1[3] (2.1)	
Totals	1[2]	2[1], 2[3]	5[1]

[1]Mosquitofish (Gambusia sp.)

[2]Crayfish (Cambarus sp.)

[3]Bluegill (Lepomis sp.)

Numbers in parentheses indicate dieldrin in ppb. All others are trace amounts.

TABLE 14. TEMPORAL DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE PANTHER BRANCH AQUATIC ECOSYSTEM SOIL/WATER (PPB) 7/1/74 to 5/31/75

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
P-04	1.1/2.1	1.8/1.0	Tr/.21	1.5/.22	1.1/.17	1.3/.20	1.1/.24	1.5/.35	1.2/.43	.92/.43
P-10	.80/.21	1.4/.31	1.0/.19	1.3/.16	1.0/.15	1.0/.13	.81/.17	2.1/.19	1.7/.23	.82/.19
P-20	2.1/.31	1.7/.22	1.1/.15	.74/.19	.86/.17	1.0/.14	0.5/.16	2.0/.70	1.7/.31	.91/.23
P-30	1.0/.35	.86/.22	.69/.20	1.0/.29	.89/.30	1.0/.21	.75/.38	1.6/.29	1.1/.26	.21/.39
S-10	2.1/.31	Tr/Tr	Tr/.11	Tr/.17	1.0/.20	1.0/.15	1.4/.17	3.1/.21	3.6/.19	2.1/.53
Lake A	.75/.21	.53/Tr	.42/.15	1.0/.19	.29/.20	1.2/.20	.51/.16	.70/.51	.73/.61	1.0/.42
Lake B	1.1/.75	.88/.51	.66/.31	.53/.29	.79/.32	1.2/.41	0.7/.38	.90/.36	.81/.72	1.2/.93
Golf Pond	1.0/.29	.62/.26	.49/.21	Tr/.19	Tr/.18	.49/.23	Tr/.17	1.1/.26	1.1/1.4	1.2/1.6
Golf Ditch	1.7/.50	1.0/.42	1.2/.20	1.1/.17	1.3/.13	1.1/.31	1.2/.21	1.0/.51	1.7/1.3	1.5/1.3

Average of 3 samples per entry (540 samples analyzed)

Tr = Trace

TABLE 15. TEMPORAL DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE PANTHER BTANCH AQUATIC ECOSYSTEM CAMBARUS SP. (CRAYFISH) (PPB) 7/1/74 to 5/31/75

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
P-04	5.1[1]	3.1	2.4					3.1[1]	2.1[1]	2.3[1]
P-10			1.3	1.0					1.3[1]	1.1[1]
P-20	2.3	2.3[1]		4.9[1]				5.3[1]	2.1[1]	3.1
P-30	6.3	4.1	1.9					4.9[1]	3.6[1]	1.8[1]
S-10	4.3	3.1[1]	3.7					2.3[1]	1.7[1]	Tr
Lake A			3.6					4.3[1]	2.1[1]	Tr
Lake B	3.1[1]	2.6							3.6[1]	2.1[1]
Golf Pond	1.3	1.7[1]	3.1				1.7[1]	1.5[1]	2.1[1]	1.0
Golf Ditch	1.9	2.7	4.3[1]	3.2[1]			1.7[1]	1.9[1]	2.3[1]	Tr

[1]Average of 3 samples per entry. Unmarked entries indicate less than 3 samples. (Total of 121 samples analyzed.)

Tr = Trace

TABLE 16. TEMPORAL DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE PANTHER BRANCH AQUATIC ECOSYSTEM GAMBUSIA SP. (MOSQUITOFISH) (PPB) 7/1/74 to 5/31/75

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
P-04	1.3[1]	1.3[1]	1.0[1]	.71[1]				1.3[1]	1.1[1]	.82[1]
P-10	1.1	1.7	.91	.61					.82	1.3
P-20	2.1	.83	1.3	1.3				Tr	Tr	1.3
P-30	1.3	.72	2.3	3.1	Tr			1.1	.81	Tr
S-10	1.0	.91	Tr	Tr	Tr				1.5	3.9[1]
Lake A	[2]	1.1	.83	Tr	Tr					Tr
Lake B	1.2[1]	1.3[1]	1.2[1]	.9				3.1[1]	2.6[1]	1.9
Golf Pond	.78[1]	2.6	1.3	1.3[1]	.81			1.9[1]	1.3	2.1[1]
Golf Ditch	.81[1]	1.3[1]	2.3[1]	3.1[1]	3.1[1]			2.8[1]	1.2[1]	5.7[1]

[1]Average of 3 samples per entry. Unmarked entries indicate less than 3 samples. (Total of 140 samples analyzed.)

[2]No collections made - blank

Tr = Trace

TABLE 17. TEMPORAL DISTRIBUTION OF MIREX IN THE PANTHER BRANCH AQUATIC ECOSYSTEM
WATER (PPB) 7/1/74 to 5/31/75

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
P-04										
P-10										
P-20										
P-30										
S-10										
Lake A										
Lake B										Tr
Golf Pond								1.3	.63	.51
Golf Ditch								1.2	.33	.21

Average of 3 samples per entry (same samples as in Table 14).

Tr = Trace

TABLE 18. TEMPORAL DISTRIBUTION OF CHLORDANE IN THE PANTHER BRANCH AQUATIC ECOSYSTEM WATER (PPB) 7/1/74 to 5/31/75

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
P-04										
P-10										
P-20										
P-30			Tr	Tr		Tr				
S-10										
Lake A			2	2	1	Tr				
Lake B			4	2	Tr	Tr				
Golf Pond	15	13	10	5	.5	.2	Tr	Tr	Tr	
Golf Ditch	19	17	16	12	8	1	.5	Tr	Tr	

Average of 3 samples per entry (same samples as in Table 14).

Tr = Trace

TABLE 19. TEMPORAL DISTRIBUTION OF MIREX IN THE PANTHER BRANCH AQUATIC ECOSYSTEM
GAMBUSIA SP. (MOSQUITOFISH) (PPB) 7/1/74 to 5/31/75

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
P-04	0[1]	0	0	0				0	0	0
P-10	0	0	0	0					0	0
P-20	0	0	0	0				0	0	0
P-30	0	0	0	0	0			0	0	0
S-10	0	0	0	0	0				0	0
Lake A	[2]	0	0	0	0					0
Lake B	0	0	0	0				0[3]	0	1.9
Golf Pond	0	0	0	0	0			2.1[3]	3.2	2.6[3]
Golf Ditch	0	0	0	0	0			3.7[3]	3.9[3]	3.9[3]

[1] No mirex recovered

[2] No collections made - blank

[3] Average of 3 samples per entry. Unmarked entries indicate less than 3 samples. (Total of 140 samples - see Table 16.)

TABLE 20. TEMPORAL DISTRIBUTION OF CHLORDANE IN THE PANTHER BRANCH AQUATIC ECOSYSTEM *CAMBARUS* SP. (CRAYFISH) (PPB) 7/1/74 to 5/31/75

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
P-04	0[1]	0	0					0	0	0
P-10	[2]		0	0						0
P-20	0	0		0				0	0	0
P-30	0	0	9					0	0	0
S-10	0	0						0	0	0
Lake A			11					0	0	0
Lake B	0	0	23						0	0
Golf Pond	22	20[3]	13				11[3]	16[3]	11[3]	11[3]
Golf Ditch	32	41	22[3]	12[3]			17[3]	19[3]	21[3]	9[3]

[1] No chlordane recovered

[2] No collections made - blank

[3] Average of 3 samples per entry. Unmarked entries indicate less than 3 samples. (Total of 121 samples.)

TABLE 21. TEMPORAL DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE WOODLANDS AQUATIC ECOSYSTEM SOIL/WATER (PPB) 6/1/75 to 12/15/76

	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Lake A	1.1[1]/Tr	1.3/Tr	0.9/Tr	0.9/ -	- / -	- / -	Tr/ -
Lake B	1.2/ -	1.1/Tr	1.0/ -	1.1/ -	Tr/Tr	Tr/ -	Tr/ -
Golf Course	0.9/ -	1.1/ -	Tr/ -	Tr/ -	0.9/ -	Tr/ -	Tr/ -
P-30	1.0/Tr	1.4/Tr	1.7/0.5	0.9/0.6	1.0/0.5	Tr/Tr	0.9/Tr

1 Average of three samples per entry

Tr = Trace

- = Not detected

TABLE 22. TEMPORAL DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE WOODLANDS AQUATIC ECOSYSTEM GAMBUSIA SP. (MOSQUITOFISH) (PPB)
6/1/75 to 12/15/76

	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Lake A	Tr	Tr	Tr	-	-	-	-
Lake B	1.3[1]	0.9	Tr	-	-	Tr	-
P-30	Tr	Tr	Tr	-	Tr	Tr	Tr

[1] Average of three samples per entry

Tr = Trace

- = Not detected

TABLE 23. TEMPORAL DISTRIBUTION OF MIREX IN THE WOODLANDS ECOSYSTEM
SOIL/WATER (PPB) 6/1/75 to 12/15/76

	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Lake A	Tr/1.1[1]	Tr/1.3	1.2/1.2	Tr/0.9	1.0/Tr	Tr/0.8	- /Tr
Lake B	Tr/1.9	1.3/0.7	2.1/1.6	1.2/1.2	1.0/1.1	0.9/Tr	Tr/Tr
Golf Course	2.1/1.7	1.9/1.6	3.1/1.9	2.9/0.9	3.1/0.8	2.1/1.3	1.3/0.7
P-30	Tr/Tr	Tr/0.8	1.3/0.9	1.1/0.8	1.7/1.0	Tr/Tr	Tr/Tr

[1] Average of samples indicated in Table 21

Tr = Trace

- = Not detected

TABLE 24. TEMPORAL DISTRIBUTION OF CHLORDANE IN THE WOODLANDS AQUATIC ECOSYSTEM SOIL/WATER (PPB) 6/1/75 to 12/15/76

	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Lake A	2.2[1]/0.9	2.4/1.0	1.7/1.2	2.1/Tr	1.3/ -	Tr/ -	Tr/ -
Lake B	1.9/Tr	1.6/2.1	1.3/1.1	2.2/Tr	1.1/Tr	0.9/ -	Tr/Tr
Golf Course	3.1/1.3	2.9/1.7	3.7/1.9	1.1/1.0	2.1/Tr	1.0/ -	0.8/Tr
P-30	Tr/Tr	Tr/ -	Tr/ -	- / -	- / -	- / -	- / -

[1] Average of samples indicated in Table 21

Tr = Trace

- = Not detected

TABLE 25. TEMPORAL DISTRIBUTION OF MIREX/CHLORDANE IN GAMBUSIA SP. (MOSQUITOFISH) FROM THE WOODLANDS AQUATIC ECOSYSTEM (PPB) 6/1/75 to 12/15/76

	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Lake A	1.1[1]/2.1	1.3/1.9	Tr/4.3	1.2/3.9	Tr/4.1	Tr/2.1	Tr/0
Lake B	2.1/5.1	1.7/3.8	1.3/4.8	1.0/5.3	Tr/4.2	- /4.1	Tr/1.2
Golf Course	3.7/6.1	3.8/5.2	4.7/6.1	5.6/4.9	4.3/5.1	3.8/3.7	2.1/0
P-30	Tr/Tr	Tr/1.3	1.3/2.1	2.1/5.1	1.3/6.1	- /0	Tr/0

[1] Average of samples indicated in Table 22

Tr = Trace

- = Not detected

0 = No sample